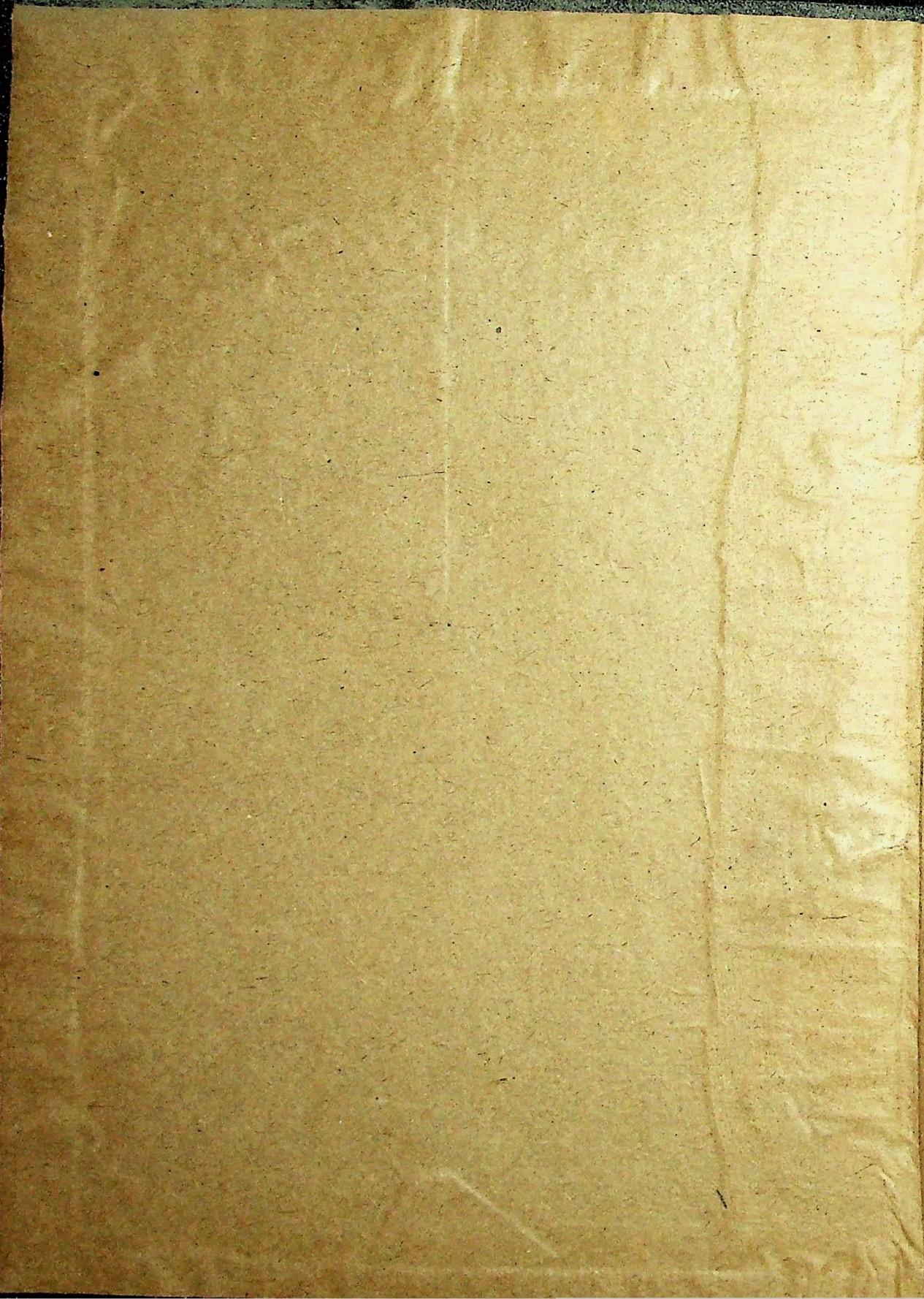


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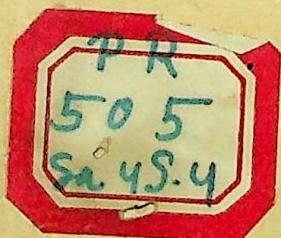
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# Sambalpur University Journal

(SCIENCE AND TECHNOLOGY)

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Vol. IV

December, 1971

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पुस्तकालय



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विषय संख्या

पुस्तक संख्या

आगत पञ्जिका संख्या

पुस्तक पर किसी प्रकार का निशान  
लगाना वर्जित है। कृपया १५ दिन से प्रधिक  
समय तक पुस्तक अपने पास न रखें। ४८३

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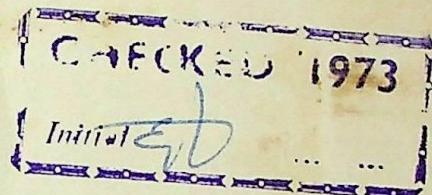
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# Sambalpur University Journal

(SCIENCE AND TECHNOLOGY)



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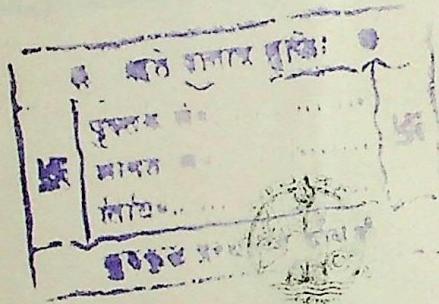
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## EDITORIAL

THE third issue of the Journal came out in July, 1971 and this is the fourth issue.

An important change has been introduced in the University Journal this time. The Science and Technology Section and the Humanities section have been separated into two different volumes to facilitate easy and proper distribution.

The University has at present 120 candidates (teachers and full-time research scholars taken together) who have registered for their Ph. D. degree. The University Regulations permit publication of research papers based on the Ph. D. thesis materials and before the thesis is submitted to the University. It is, therefore, natural that most of the scholars prefer to publish their articles containing original thoughts in journals reputed in the specific fields of knowledge and which have a very wide circulation both within the country and abroad. Delay in publication of the University Journal also becomes an important factor for the scholars to hesitate in contributing their research articles to this journal as in the competitive world of research today there is the possibility of the same problem being worked out at different centres of research and delay in publication of the result may make a world of difference between two similar works. The articles published in the University Journal, therefore, may not reflect the true standard of work that is being done by the scholars of the University to-day. Yet, articles published in this volume will, I am sure, be of great interest to the scholars of the respective fields working in other Universities and research centres. It is hoped that time will soon come when due to the wide circulation of this journal and its timely publication, our scholars will consider this journal as one of the best forums for publishing their papers.

B. BEHERA

*Editor-in-Chief*



মুদ্রকালী

বৃহত্তর পৰিভৰ্তা বিদ্যালয়

শ্ৰীগুৱা

## THE GENERALISED [N, p, q] SUMMABILITY

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(Received 7 December 1970)

### 1. Notations and definitions :

The (N, p, q) transform (\*) of  $S_n = \sum_{v=0}^n a_v$  is defined by

$$f_n = \frac{\sum_{v=0}^n p_{n-v} q_v s_v}{r_n},$$

where,

$$r_n = \sum_{v=0}^n p_v q_{n-v}, \quad (p_{-1} = q_{-1} = r_{-1} = 0)$$

$\neq 0$  for  $n \geq 0$ .

The series  $\sum_{n=0}^{\infty} a_n$  or the sequence  $\{s_n\}$  is said to be summable (N, p, q) to  $s$ , if,  $f_n \rightarrow s$  as  $n \rightarrow \infty$ , and is said to be absolutely summable | N, p, q |, if,  $\{f_n\} \in \text{BV}$  and when this happens, we shall write symbolically by  $\{S_n\} \in |N, p, q|$ .

The method (N, p, q) reduces to the method (N, p) when  $q_n = 1$ , [Hardy [4], 64] ; to the method (N, q) when  $p_n = 1$ , ([4], 57) ; to the Euler—Knopp method (E,  $\delta$ ) when  $p_n = \frac{\alpha^n \delta^n}{n!}$ ,  $q_n = \frac{\alpha^n}{n!}$  ( $\alpha > 0$ ,  $\delta > 0$ ) ([4], 178) ; to the method (C,  $\alpha$ ,  $\beta$ ), [Borwein (1)], when  $p_n = \binom{n+\alpha-1}{\alpha}$ ,  $q_n = \binom{n+\beta}{\beta}$ .

We write,

$$\lambda_n = p_n - p_{n-1}$$

$$\mu_n = Q_n^\alpha$$

and  $\chi_n = \sum_{v=0}^n \lambda_{n-v} Q_v^\alpha.$

2. The object of the present paper is to introduce a new method of summability and study some of its relevant aspect in reference of Das ([2], [3]).

(\*) Borwein (1), This is called the generalized Norlund Transform.

We note that,

$$r_n = \sum_{v=0}^n p_{n-v} q_v = \sum_{v=0}^n \lambda_{n-v} Q_v, (\sum_{v=0}^n q_v = Q_n)$$

and,

$$\begin{aligned} \sum_{v=0}^n p_{n-v} q_v s_v &= \sum_{v=0}^n (p_{n-v} - p_{n-v-1}) \sum_{\mu=0}^v q_{\mu} s_{\mu} \\ &= \sum_{v=0}^n \lambda_{n-v} t_v Q_v \end{aligned}$$

where,

$$t_v = \frac{1}{Q_v} \sum_{\mu=0}^v q_{\mu} s_{\mu} = \frac{1}{Q_v} \sum_{\mu=0}^v (Q_v - Q_{\mu-1}) a_{\mu} \text{ if } \lambda_n = p_n - p_{n-1}.$$

Here  $\{t_v\}$  is the  $(\bar{N}, q)$  mean [[4], p. 57] which is equivalent to  $(R^*, Q_{n-1}, 1)$  mean [[4], p. 113].

Re-writing  $f_n$  in terms of the simplification given above, we now have,

$$f_n = \frac{\sum_{v=0}^n (p_{n-v} - p_{n-v-1}) t_v Q_v}{\sum_{v=0}^n (p_{n-v} - p_{n-v-1}) Q_v}$$

and this form suggests that we can have the following extension of the  $(N, p, q)$  method.

We now write, for any  $\{\lambda_n\}$ ,

$$f_n^{(a)} = \frac{\sum_{v=0}^n \lambda_{n-v} t_v^{(a)} \mu_v}{\sum_{v=0}^n \lambda_{n-v} \mu_v}, \quad (2.1)$$

where

$$t_n^{(a)} = \frac{1}{Q_n} \sum_{v=0}^n (Q_n - Q_{v-1})^a a_v. \quad (2.2)$$

We denote this mean by  $G(N, p, q)$ . It may be noted that,  $t_v^{(a)}$  is the  $(R^*, Q_{n-1}, a)$  mean or the Discontinuous Riesz mean of the type  $Q_n$  and order  $a$  of  $\{S_n\}$ ; and hence,  $f_n^{(a)}$  is the  $(N, \lambda, \mu)$  mean of the  $(R^*, Q_{n-1}, a)$  mean of  $S_n$ .

When  $a=1$ ,

$$f_n^{(1)} = (N, p, q) (S_n).$$

Again, when  $\lambda_0=1, \lambda_n=0$  for  $n \geq 1$  and  $\mu_n=1$ ,  $(N, \lambda, \mu)$  is the Identity transformation of  $S_n$  and hence in this case  $f_n^{(a)}$  is the  $(R^*, Q_{n-1}, a)$  transformation.

The Summability  $G(N, p, q)$  and  $|G(N, p, q)|$  are defined in the usual manner.

3. In a recent paper Das [3] introduced the following method :

Let,

$$J_k(z) = \left( \sum_{n=0}^{\infty} Q_n^k z^n \right)^{-1} \sum_{n=0}^{\infty} z^n \sum_{v=0}^n (Q_n - Q_{v-1})^k a_v,$$

where,

$$\sum_{n=0}^{\infty} Q_n^k z^n \text{ and } \sum_{n=0}^{\infty} z^n (Q_n - Q_{v-1})^k a_v,$$

are convergent for  $|z| < f_k$ .

If,  $J_k(x) \rightarrow v$  as  $x \rightarrow f_k$ —(through positive values) then  $\{S_n\}$  is said to be summable (J, q, k) to v. Absolute summability  $|J, q, k|$  is defined when,

$$\int_0^{f_k-1} |d J_k(x)| < \infty.$$

When  $|Z| < 1$  and  $k=1$ , it is known Das [3] that, (J, q, k). Is the same as (J, q), {for (J, q) method, see [4], p. 79}. If  $k=0$  and  $Q_k - Q_{v-1} \neq 0$ , then the  $J_k(x)$  mean is the Abel mean ; and in the case  $Q_n - Q_{v-1} = 0$ ,  $(Q_n - Q_{v-1})^k$  may be defined as 1, so that the  $J_k(x)$  mean is defined.

The following theorems are known [3].

#### Theorem A

In order that  $(R^*, Q_{n-1}, k)$  should imply  $(J, q, k)$ , it is necessary and sufficient that the condition  $\sum_{n=0}^{\infty} Q_n^k x^n \rightarrow \infty$  as  $x \rightarrow f_k-$ , should hold.

#### Theorem B

If  $\sum a_n$  is summable  $|R^*, Q_{n-1}, k|$  to s, then it is summable  $|J, q, k|$  to the same sum. Before going to establish our theorems, we now consider the regularity of the G(N, p, q) method.

#### 4. Regularity :

From the transformation (2.1) we get,

$$\begin{aligned} \mathfrak{J}_n^{(a)} &= \frac{1}{x_n} \sum_{v=0}^n \lambda_{n-v} \sum_{\mu=0}^n \{(Q_v - Q_{\mu-1})^a - (Q_v - Q_\mu)^a\} a \mu \\ &= \frac{1}{x_n} \sum_{\mu=0}^n S_\mu \sum_{v=\mu}^n \lambda_{n-\mu} \{(Q_v - Q_{v-1})^a - (Q_v - Q_\mu)^a\} \\ &= \sum_{\mu=0}^n S_\mu \beta_{nv}, \end{aligned}$$

where,

$$\beta_{nv} = \begin{cases} \frac{\sum_{v=\mu}^n \lambda_{n-v} \{(Q_v - Q_{v-1})^a - (Q_v - Q_\mu)^a\}}{x_n}, & (\mu \leq n) \\ 0 & (\mu > n) \end{cases} \quad (4.1)$$

and therefore the necessary and sufficient conditions of regularity of  $G(N, p, q)$  are,

$$\beta_{nv} = o(1) \text{ as } n \rightarrow \infty \quad (v, \text{ fixed}) \quad (4.2)$$

$$\text{and, } \sum_{v=0}^n |\beta_{nv}| = O(1) \quad (4.3)$$

It is difficult to find out simpler conditions for which (4.2) and (4.3) to be satisfied. We therefore follow the indirect method (as discussed in Das [3]) to determine simpler conditions of regularity (and also absolute regularity). For this we consider the matrix as given in (2.1) :

The transformation matrix in (2.1) from  $t_v^{(a)}$  to  $f_v^{(a)}$  is

$$a_{nv} = \begin{cases} \frac{\lambda_{n-v} Q_v^a}{\chi_n}, & (v \leq n) \\ 0, & (v > n) \end{cases} \quad (4.4)$$

Hence the necessary and sufficient conditions for  $(R^*, Q_{n-1}, a) \subset (N, p, q)$  are, [See Hardy [4] Theorem 2].

$$\sum_{v=0}^n |\lambda_{n-v} Q_v^a| = O(\chi_n) \quad \dots \dots \dots \quad (4.5)$$

$$\text{and} \quad \lambda_{n-v} Q_v^a = o(\chi_n) \quad (n \rightarrow \infty; v, \text{ fixed}) \quad (4.6)$$

and therefore the necessary and sufficient conditions for  $|R^*, Q_{n-1}, a| \subset |G(N, p, q)|$ , [Knopp & Lorentz [5]] are (4.6) and the following :

$$J_f = \sum_{n=f}^{\infty} \left| \sum_{v=f}^n \left( \frac{\lambda_{n-v}}{\chi_n} - \frac{\lambda_{n-v-1}}{\chi_{n-1}} \right) Q_v^a \right| = o(1) \quad (4.7)$$

Condition (4.5) is satisfied, if,  $\lambda_n \geq 0, Q_n \geq 0$ . (4.8)

Condition (4.6) is equivalent to

$$\lambda_{n-v} = o(\chi_n) \text{ as } n \rightarrow \infty, \quad (v, \text{ fixed}) \quad (4.9)$$

for those values of  $v$  for which  $Q_v \neq 0$ .

Now the condition (4.9) is satisfied whenever (4.8) and the following hold :

$$\frac{\lambda_{n-v}}{Q_n^a} = o(1) \text{ as } n \rightarrow \infty, \quad (v, \text{ fixed}) \quad (4.10)$$

Thus  $(R^*, Q_{n-1}, a) \subset G(N, p, q)$ ,  
if (4.8) and (4.10) hold.

But  $(R^*, Q_{n-1}, a)$  is regular when

$$0 < Q_0 < Q_1 < \dots \dots \dots \rightarrow \infty \quad (4.11)$$

*Hence it follows that (4.8), (4.10) and (4.11) is a set of sufficient conditions of regularity of the  $G(N, p, q)$  method.*

Now let us consider the absolute regularity of the  $|G(N, p, q)|$  method.

We have,

$$\begin{aligned}
 J_f &= \sum_{n=f}^{\infty} \left| \sum_{v=f}^n \left( \frac{\lambda_{n-v}}{\chi_n} - \frac{\lambda_{n-v-1}}{\chi_{n-1}} \right) Q_v^a \right| \\
 &= \sum_{n=f}^{\infty} \left| \left( \sum_{v=0}^{f-1} - \sum_{v=0}^{f-1} \right) \left( \frac{\lambda_{n-v}}{\chi_n} - \frac{\lambda_{n-v-1}}{\chi_{n-1}} \right) Q_v^a \right| \\
 &= \sum_{n=f}^{\infty} \left| \sum_{v=0}^{f-1} \left( \frac{\lambda_{n-v-1}}{\chi_{n-1}} - \frac{\lambda_{n-v}}{\chi_n} \right) Q_v^a \right|
 \end{aligned} \tag{4.14}$$

Let (4.8) hold and let

$$\frac{\lambda_n}{\chi_n} \geqslant \frac{\lambda_{n-1}}{\chi_{n-1}}$$

Then

$$\sum_{v=0}^{f-1} \left( \frac{\lambda_{n-v-1}}{\chi_{n-1}} - \frac{\lambda_{n-v}}{\chi_n} \right) Q_v^a \geqslant 0$$

Hence it follows from (4.14) that

$$\begin{aligned}
 J_f &= \lim_{m \rightarrow \infty} \sum_{n=f}^m \sum_{v=f}^n \left( \frac{\lambda_{n-v}}{\chi_n} - \frac{\lambda_{n-v-1}}{\chi_{n-1}} \right) Q_v^a \\
 &= \lim_{m \rightarrow \infty} \sum_{v=f}^m Q_v^a \sum_{n=f}^m \left( \frac{\lambda_{n-v}}{\chi_n} - \frac{\lambda_{n-v-1}}{\chi_{n-1}} \right) \\
 &= \lim_{m \rightarrow \infty} \frac{1}{X_m} \sum_{v=f}^m Q_v^a \lambda_{m-f} \\
 &\leqslant \lim_{m \rightarrow \infty} \sum_{v=0}^n \frac{Q_v^a \lambda_{n-v}}{\chi_m} \\
 &= \lim_{m \rightarrow \infty} \frac{\chi_m}{\chi_m} = 1
 \end{aligned}$$

Since  $|R^*, Q_{n-1}, k|$  is absolutely regular when (4.12) is satisfied, we now get, (4.8), (4.11) and (4.15) as a set of sufficient conditions for absolute regularity of  $|G(N, p, q)|$

5. Let,

$$\lambda(z) = \sum_{n=0}^{\infty} \lambda_n Z^n \text{ and } \mu(z) = \sum_{n=0}^{\infty} \mu_n Z^n$$

whenever the series on the right converge and let the radii of convergence of both the series be  $\lambda$  and  $\mu$  respectively such that

- (a)  $\mu \leqslant \lambda$ ,
- (b)  $\lambda(z) = \sum_{n=0}^{\infty} \lambda_n Z^n \neq 0 (|z| < \lambda)$

We now prove the following two theorems :

Theorem 1.

Let either of the following conditions A, B or C hold.

$$A : \begin{cases} (i) \lambda_0 > 0, \lambda_n \geq 0, \mu_0 > 0, \mu_n \geq 0 \\ (ii) \lambda(x) = \sum_{n=0}^{\infty} \lambda_n x^n \rightarrow \infty, \text{ as } x \rightarrow f\mu - 0 \\ (iii) X(x) \neq 0, \text{ for } |x| < 1. \end{cases}$$

$$B : \begin{cases} (i) \lambda_0 \neq 0, \mu_0 > 0, \mu_n \geq 0, f\mu = 1, \\ (ii) X_n [X_n \neq 0] \text{ for } n \geq 0 \text{ is real and such that} \\ (iii) |X_n| \geq \delta > 0, \frac{X_n}{X_{n-1}} \rightarrow 1 \text{ as } n \rightarrow \infty \end{cases}$$

$$C : \begin{cases} (i) \lambda_0 \neq 0, \mu_0 > 0, \mu_n \geq 0, f\mu = 1, \\ (ii) X_n [X_n \neq 0, \text{ for } n \geq 0] \text{ is complex and such that} \\ (iii) X_n \rightarrow X \text{ as } n \rightarrow \infty \end{cases}$$

where  $X$  is non-zero and finite, then, if  $\sum Q_n$  is summable  $G(N, p, q)$  to  $s$ , it is summable  $(J, q, k)$  to the same sum.

Theorem 2.

Let  $X_n \neq 0, \mu_n \geq 0$ , and conditions (a) and (b) of (5.1) hold. Also let  $\phi_n(x) = \sum_{v=0}^n X_v x^v / \sum_{v=0}^{\infty} X_v x^v$  be a function of bounded variation of  $x$  in the  $(0, f\mu)$  uniformly in  $n$ . Then, if  $\sum a_n$  is summable  $|G(N, p, q)|$ , it is summable  $(J, q, k)$ .

*Proof of Theorem 1.* We proceed as in Das (3).

$$\text{Let, } T(z) = X_n f_n^{(a)} Z^n \quad (5.2)$$

$$\text{We write } X(z) = \sum_{n=0}^{\infty} X_n Z^n$$

$$\text{such that, } X(z) = \lambda(z) (\mu z) \quad (5.2)$$

Under the conditions of Theorem 1,  $\lambda(z) = \sum_{n=0}^{\infty} \lambda_n z^n$  is convergent for  $|z| < f\mu$ .

Now if  $f_n^{(a)} = 0$  (1),  $T(z)$  has a radius of convergence at least  $f\mu$ . The function  $\frac{T(z)}{\lambda(z)}$  is regular inside the circle  $|Z| < f\mu$ . If  $\lambda(z)$  has no zeros inside the circle  $|z| < f\mu$ , then  $T(z)/\lambda(z)$  is regular in  $|Z| < f'$ , where  $f'$  is the distance of the nearest zero of  $\lambda(z)$  from the origin.

Therefore,  $T(z)/\mu(z)$  is expandable in a power-series  $W(z) = \sum_{n=0}^{\infty} w_n Z^n$  which is convergent for  $|z| < f'$ . Now since  $|Z| < f'$ ,  $T(z) = \lambda(z) W(z)$ .

We then have,

$$f_n^{(a)} X_n = \lambda_0 w_n + \lambda_1 w_{n-1} + \dots + \lambda_n w_0 \quad (5.4)$$

But by definition,

$$\begin{aligned} f_n^{(a)} X_n &= \sum_{v=0}^n \lambda_{n-v} t_v^a Q_v^a \\ &= \sum_{v=0}^n \lambda_{n-v} \sum_{\mu=\delta}^{\delta} (Q_v - Q_{\mu-1})^a a \mu \\ &= \sum_{v=0}^n \lambda_{n-v} Y_v, \text{ say,} \end{aligned}$$

where,

$$Y_v = \sum_{\mu=0}^v (Q_v - Q_{\mu-1})^a a \mu$$

Therefore,

$$f_n^{(a)} X_n = \lambda_n \gamma_0 + \lambda_{n-1} \gamma_1 + \dots + \lambda_0 \gamma_n \quad (5.5)$$

On comparing (5.4) and (5.5) we now have,

$$\omega_n = \gamma_n$$

Hence,

$$\sum_{n=0}^{\infty} Y_n Z^n = \frac{\sum_{n=0}^{\infty} f_n^{(a)} X_n Z^n}{\sum_{n=0}^{\infty} \lambda_n Z^n} \quad (5.6)$$

is regular for  $|z| < f_\mu$ , except for possible poles and is convergent for  $|z| < f'$ .

Therefore,

$$\frac{\sum_{n=0}^{\infty} Y_n Z^n}{\sum_{n=0}^{\infty} \mu_n z^n} = \sum_{n=0}^{\infty} b_n Z^n$$

for suitably chosen  $b_n$ , is convergent for  $|z| < f_1$ , where  $f_1 = \min(f', f'')$  and  $f''$  is the distance of the nearest zero of  $\mu(z)$ .

Now,

for  $|z| < f_1$ , ( $f_1$  may be small),

$$J_q^k(z) = \frac{\sum_{n=0}^{\infty} Y_n Z^n}{\sum_{n=0}^{\infty} \mu_n Z^n} = \frac{\sum_{n=0}^{\infty} f_n^{(a)} X_n Z^n}{\sum_{n=0}^{\infty} \mu_n Z^n \sum_{n=0}^{\infty} \lambda_n Z^n} \quad \text{by } (5.7)$$

$$= \frac{\sum_{n=0}^{\infty} f_n^{(a)} X_n Z^n}{\sum_{n=0}^{\infty} X_n Z^n} \quad (5.8)$$

is regular except for poles.

Of course, for this the only requirement is that  $\sum_{n=0}^{\infty} Y_n x^n$  &  $\sum_{n=0}^{\infty} \mu_n x^n$  should be convergent and thus the summability G (N, p, q) gives the applicability of the (J, q, k) method.

Now the sequence to function transformation is regular [Hardy [4] Theorem 5], if and only if,

$$\sum_{n=0}^{\infty} \left| X_n \right| x^n = O \left( \sum_{n=0}^{\infty} X_n x^n \right) \text{ as } x \rightarrow f\mu \rightarrow 0$$

and  $X_n x^n = o \left( \sum_{n=0}^{\infty} X_n x^n \right)$  as  $x \rightarrow f\mu \rightarrow 0$

and these are already fulfilled under the conditions of the present theorem. The applicability of the conditions A, B or C for the sequence to function transformation is justified in the same line of proof as given in Das [2], section 5).

*Proof of Theorem 2.*

We have,  $X(x) = \sum_{n=0}^{\infty} X_n x^n$

and let,  $T(x) = \sum_{n=0}^{\infty} X_n f_n^{(a)} x^n$

and  $f(x) = T(x)/X(x)$ .

We have by hypothesis,  $X(x)$  has a radius of convergence  $f\mu$  and,

$$\sum_{n=0}^{\infty} \left| f_n^{(a)} - f_{n-1}^{(a)} \right| < \infty ;$$

hence  $f_n^{(a)}$  tends to a finite limit, therefore  $T(x)$  has a radius of convergence  $f\mu$ . Then proceeding according to [6] McFadden (1942), we can write,

$$\begin{aligned} \int_0^{f\mu} |f'(x)| dx &= \int_0^{f\mu} \left| \sum_{n=0}^{\infty} \phi_n^1(x) \left( f_n^{(a)} - f_{n-1}^{(a)} \right) \right| dx \\ &= \sum_{n=0}^{\infty} |f_n^{(a)} - f_{n-1}^{(a)}| \int_0^{f\mu} |\phi_n^1(x)| dx \\ &\leq C \sum_{n=0}^{\infty} |f_n^{(a)} - f_{n-1}^{(a)}| \\ &\leq C \end{aligned}$$

where C is a finite positive constant not necessarily the same at each occurrence.

And this is the condition that,

$$\sum_{n=0}^{\infty} a_n \text{ is summable } (J, q, k) .$$

Thus Theorem 2 is proved.

At last I express my grateful thanks to Dr. G. Das for his valuable guidance in this paper.

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## FUNCTIONAL CLASSIFICATION OF URBAN AREAS IN THE STATE OF ORISSA

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In this paper an attempt has been made to classify the urban areas in the State of Orissa by analysing the proportion of labour force engaged in various activity groups. The arithmetic mean of the percentage of labour force for the whole State has been taken as the criterion of classification. Analyses of the frequency distribution of services and spatial distribution of urban areas according to functional grouping have been presented here.

### INTRODUCTION

A N urban area is a multifunctional human settlement serving its inhabitants as well as the region in which it is located. The size of a city is influenced by the functions it performs.<sup>1</sup> The relationship with the region dictates the functional specialization of the urban area.

The role of a city in the region can be best understood by analysing the functions it performs. The city-forming functions are of greater significance than the city-serving ones for the aforesaid analysis. This will also give an insight to the economic base of the city. "Determination of the extent to which each of the urban functions serves the population out-side the city, in contrast to the production of goods and services for consumption inside the city, is an important part of most studies of the urban economic base."<sup>2</sup>

The paper presents a functional classification of 5,000+ urban areas in the State of Orissa. This State comprises of an area of 155,843 sq. km. and a population (1961 census) of 17,548,846.<sup>3</sup> According to 1961 Census, there are fifty-nine urban areas having population more than 5,000.<sup>4</sup>

### METHODOLOGY

The nature and extent of the functions a city performs can be recognised either by the spatial distribution and occupancy or by the labour force absorbed in each function. Since the spatial distribution and occupancy depend more on the topography, transportation facilities and availability of resources, it cannot be used as a criterion for comparison between two cities. Harris,<sup>5</sup> Nelson<sup>6</sup> and Pownall<sup>7</sup> have advocated for the analysis of labour force engaged in different services in connection with the functional classification of cities.

In this paper the author has followed the technique adopted by Nelson. The census reports<sup>8</sup> provide the required informations regarding population and occupational structure of the urban areas. The following categories of occupational pattern have been taken into account for analysis.

- (i) Cultivation and agricultural labour.
- (ii) Mining, quarrying, livestock, forestry, fishing, hunting and Plantations, orchards and allied activities.
- (iii) Household industry.
- (iv) Manufacturing other than household industry.
- (v) Trade and commerce.
- (vi) Transport, storage and communication.

Agriculture does not give urban characters to a settlement. As has been pointed out by Bergel<sup>9</sup>, a settlement can be called an urban area where the majority of the occupants are engaged in activities other than agriculture. The urban areas in this region have not advanced much in the direction of industrial development. Moreover, agricultural land is found in the close vicinity of almost all these urban areas. Hence it is relevant to take into account 'Agriculture' as an urban function in the present context.

For each urban area, percentages of labour force in different occupations have been determined. The arithmetic mean and standard deviation for each occupation and for all the urban areas have been found out. For a particular urban area, the percentage of workers engaged in a particular occupation has been compared with the arithmetic mean and standard deviation for all the urban areas. Accordingly its place in the classification table is determined. An urban area may have these percentages in different occupations higher than the average and accordingly may show the significance of more than one class of function. The urban areas which have the working force less than the arithmetic average in all the groups of activities have been classified as 'Diversified'. In a diversified urban area none of the activities is significantly dominant.

The classification has been given in the Table No. 1.

TABLE I—FUNCTIONAL CLASSIFICATION OF 5,000+ URBAN AREAS OF  
THE STATE OF ORISSA

Function	K E Y			
	Between average and average + I.S.D	Between average + I.S.D and average + 2 S.D.	Between average + 2 S.D. and average + 3 S.D.	Above average + 3 S.D.
Cultivation, Agricultural labour	<i>Ag</i>	<i>Ag1</i>	<i>Ag2</i>	<i>Ag3</i>
Mining, quarrying, livestock, forestry, fishing, hunting, and plantations, orchards and allied activities	<i>Pr</i>	<i>Pr1</i>	<i>Pr2</i>	<i>Pr3</i>
House-hold industries	<i>Ih</i>	<i>Ih1</i>	<i>Ih2</i>	<i>Ih3</i>
Manufacturing other than house-hold industries	<i>Im</i>	<i>Im1</i>	<i>Im2</i>	<i>Im3</i>
Trade and Commerce	<i>Tc</i>	<i>Tc1</i>	<i>Tc2</i>	<i>Tc3</i>
Transport, storage and communications	<i>Ts</i>	<i>Ts1</i>	<i>Ts2</i>	<i>Ts3</i>
Diversified	<i>D</i>			

Urban area	Population	Classification			
Cuttack	146,308	<i>Ih</i>	<i>Im</i>	<i>Tc</i>	<i>Ts</i>
Rourkela	90,287	<i>Im1</i>	<i>Ts</i>		
Berhampur	76,931	<i>Ih</i>	<i>Im</i>	<i>Tc</i>	<i>Ts</i>
Puri	60,815	<i>Pr</i>	<i>Tc</i>	<i>Ts</i>	
Sambalpur	38,915	<i>Ih</i>	<i>Im</i>	<i>Tc</i>	<i>Ts</i>
Bhubaneswar	38,221	<i>D</i>			
Balasore	33,931	<i>Im</i>			
Jeypore	25,291	<i>Im</i>	<i>Tc</i>		<i>Ts</i>
Bhadrak	25,285	<i>Im</i>		<i>Tc</i>	
Parlakhemundi	22,708	<i>Pr</i>	<i>Ih</i>	<i>Tc</i>	
Baripada	20,301	<i>Ih</i>	<i>Im</i>		
Birmitrapur	20,301	<i>Pr3</i>			
Barbil	19,340	<i>Pr1</i>	<i>Im</i>	<i>Ts1</i>	
Jharsuguda	19,227	<i>Im</i>	<i>Tc</i>	<i>Ts2</i>	
Bolangir	18,663	<i>Ih</i>	<i>Ts</i>		
Brajarajnagar	16,196	<i>Pr1</i>	<i>Im3</i>		
Jatni	16,068	<i>Tc</i>	<i>Ts3</i>		
Kendrapara	15,830	<i>Ih</i>	<i>Im</i>	<i>Tc</i>	
Angul	15,738	<i>Ag1</i>			
Bargarh	15,375	<i>Pr</i>	<i>Tc</i>		
Rayagada	14,537	<i>Pr</i>	<i>Tc</i>		
Bhawanipatna	14,300	<i>Tc</i>			
Rajgangpur	13,843	<i>Ag</i>	<i>Im2</i>	<i>Tc</i>	
Jajpur	13,802	<i>Pr</i>	<i>Ih</i>	<i>Tc</i>	
Dhenkanal	13,727	<i>Ih</i>			
Chowduar	13,478	<i>Im3</i>			
Soro	13,081	<i>Ag2</i>	<i>Im</i>		
Keonjhar	12,624	<i>Ag</i>			
Khurda	12,497	<i>Ag</i>	<i>Tc</i>		
Sundargarh	11,329	<i>Ag</i>			
Nowrangpur	10,380	<i>Tc</i>			
Burla	10,230	<i>D</i>			
Jaleswar	10,202	<i>Ag2</i>			
Gunupur	10,180	<i>Ih</i>	<i>Tc</i>		
Bhanjanagar	9,952	<i>Ih</i>	<i>Tc</i>		
Bhuban	9,476	<i>Ag2</i>	<i>Ih2</i>	<i>Tc</i>	
Chandbali	9,406	<i>Ag1</i>			
Aska	9,024	<i>Ag</i>	<i>Ih1</i>		
Kantabanji	8,863	<i>Tc</i>	<i>Ts2</i>		
Suruda	8,703	<i>Pr1</i>	<i>Ih</i>	<i>Tc</i>	<i>Ts1</i>
Hirakud	8,593	<i>Im</i>			
Talcher	8,147	<i>Pr</i>	<i>Ih</i>		
Rairangapur	8,119	<i>Ag1</i>			
Hinjili	8,028	<i>Ag1</i>	<i>Pr</i>	<i>Ih1</i>	
Khariar	7,873	<i>Ag</i>	<i>Pr</i>	<i>Tc</i>	
Chatrapur	7,835	<i>D</i>			
Patnagarh	7,592	<i>Ag1</i>	<i>Ih1</i>		
Koraput	7,461	<i>D</i>			

Urban area	Population	Classification		
Titlagarh	7,433	<i>Tc</i>	<i>Ts</i>	
Athgarh	7,256	<i>Ag</i>		
Sonepur	7,108	<i>Pr</i>	<i>Ih3</i>	<i>Tc</i>
Deogarh	6,839	<i>Ag</i>		
Khariar Road	6,400	<i>Ag1</i>		
Kotpad	6,368	<i>Tc</i>		
Baudh	6,088	<i>Pr</i>	<i>Ih2</i>	<i>Tc</i>
Jajpur Road	5,989	<i>Ag</i>	<i>Tc</i>	<i>Ts1</i>
Banki	5,934	<i>Ag1</i>		
Nayagarh	5,815	<i>Ag1</i>	<i>Ih</i>	
Bellaguntha	5,762	<i>Ag</i>	<i>Pr</i>	<i>Ih2</i>
				<i>Tc</i>

#### FREQUENCY DISTRIBUTION OF SERVICES

The figures nos. 1 and 2 are graphical representation of distribution of services in the urban areas under study. Most of the graphs indicate 'peaking' at a lower percentage of labour force whereas few others show either fairly uniform distribution or 'peaking' near the average. None of the frequency variation graphs shows grouping at a particular percentage.

#### SPATIAL DISTRIBUTION OF URBAN AREAS ACCORDING TO FUNCTIONAL GROUPS

In Orissa, most of the urban centres are on the main transportation routes. The largest centre i. e., Cuttack lies on the head of the delta of River Mahanadi. Except few small ones, there is no urban centre in the central part of the State.

Almost all urban centres having significance in cultivation and agricultural labour lie in two bands, one running parallel to the coast and the other on the north-western boundary of the State (Fig. No. 3). This is indicative of the availability of agricultural land and good irrigation facilities in those areas.

The urban centres where mining, fishing, hunting etc., are dominant, lie almost in a band running in NW-SE direction in the centre of the State extending from the coast to the western border (Fig. No. 4). The absence of urban areas specialised in activities other than household industries indicates the necessity of exploration of natural resources in this zone.

Most of the urban centres with significant percentage of labour force engaged in household industry lie close to the coastal tract (Fig. No. 5). Some such centres also lie in the western Orissa.

Orissa has few centres where manufacturing industry is a significant function (Fig. No. 6). Except Berhampur and Rayagada in the south all

such centres are in the northern and western parts of the State. These centres are situated on the main rail routes and on National or State Highways. Proximity of a good market in Eastern India and the supply of raw materials from western Orissa, Bengal and Bihar have supported the industrial centres in the north-western parts of the State.

The urban centres having significant labour force engaged in Trade and Commerce are widely distributed throughout the State (Fig. 7). Since the percentage of labour force engaged in this activity group is not very high in most of the urban centres, there is an indication that these centres serve small hinterlands.

There are fourteen urban centres in the State where the percentage of labour force engaged in Transport, Storage and Communication is higher than the State average (Fig. No. 8). These centres lie on two bands, one parallel to the Howrah-Madras railway line running along the coast, and the other in western Orissa running parallel to Jharsuguda-Titlagarh railway line. This group of activities is also significant in most of the trade centres.

Three of the four 'diversified' urban centres in the State are administrative towns and the fourth (i. e., Burla is a seat of educational Institutions (Fig. No. 9).

#### CONCLUSIONS

1. Agriculture is a significant function in most of the urban areas of the State.
2. Most of the urban centres bank more on 'Trade and Commerce and/or Household industry' rather than on manufacturing industry or Transport, Storage and Communication.'
3. The urban areas having 'agriculture' as a significant function are also commercial centres of significance.
4. The spatial distribution of urban centres is as follows :

(i) Agriculture significant	.. Along the costal tract of the State.
(ii) Mining etc. significant	.. Central zone of the State extending from the coast to western boarder.
(iii) Household industry significant	Along the coast and in western Orissa.
(iv) Manufacturing Industry significant	In North-Western part of the State.
(v) Trade and Commerce significant	Throughout the State except a part of North Orissa.
(vi) Transport, Storage, and Communication significant ..	Along the main routes of transportation.

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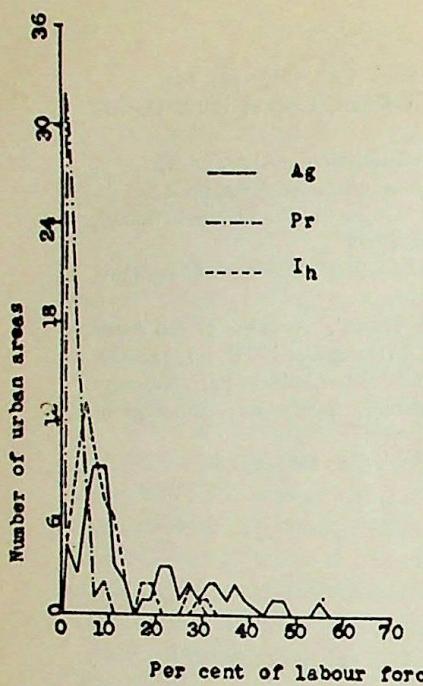


FIG. 1

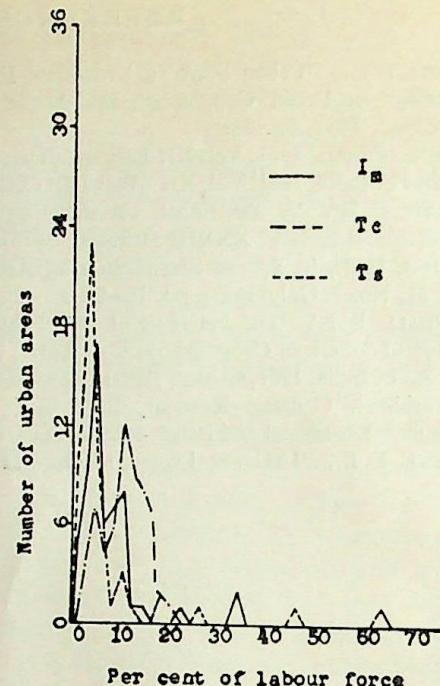


FIG. 2

## DISTRIBUTION OF ECONOMIC ACTIVITIES

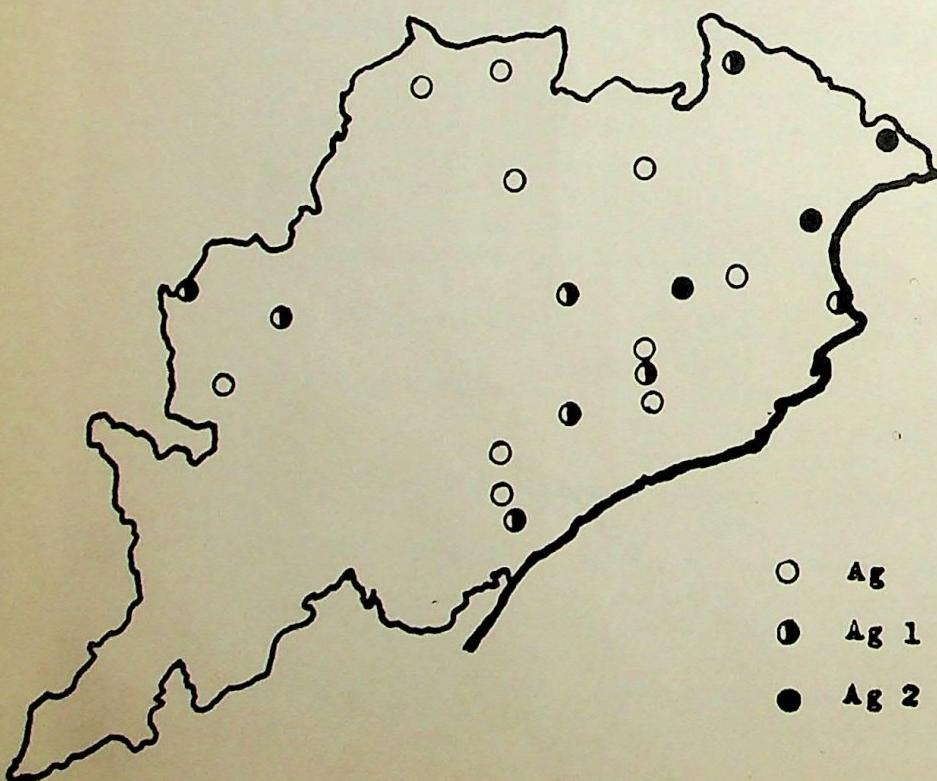


FIG. 3-Cultivation and Agricultural labour

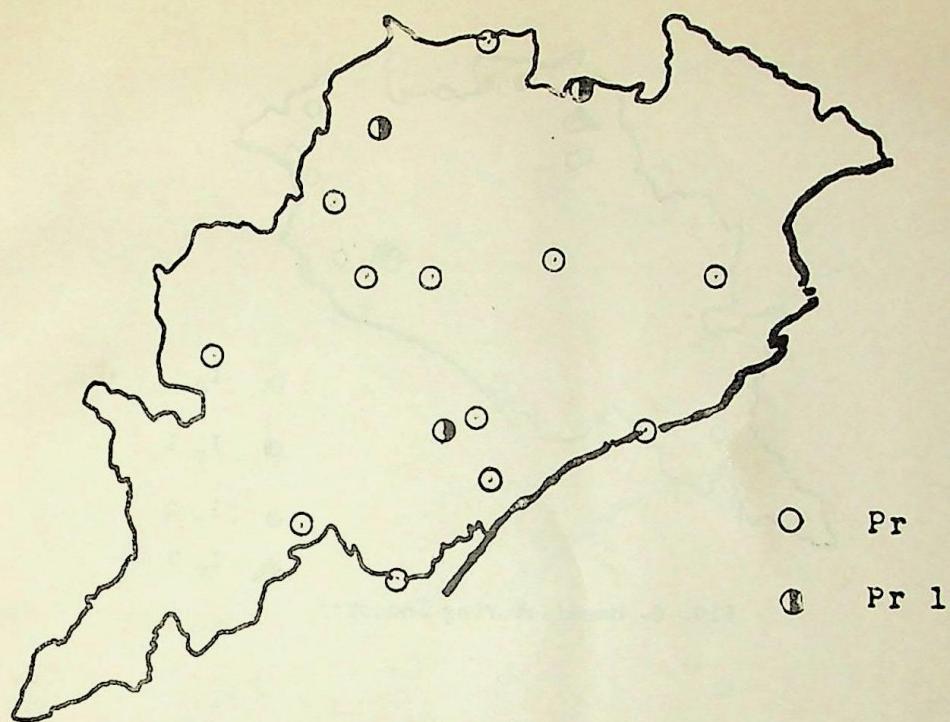


FIG. 4- Mining, hunting etc.

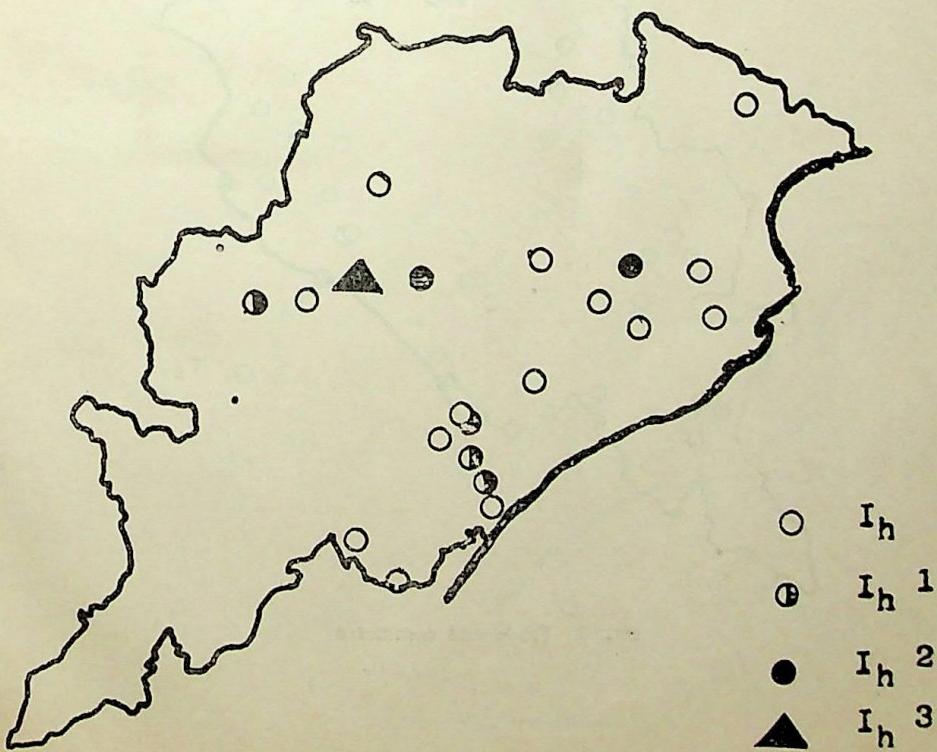


FIG. 5 - Household Industry

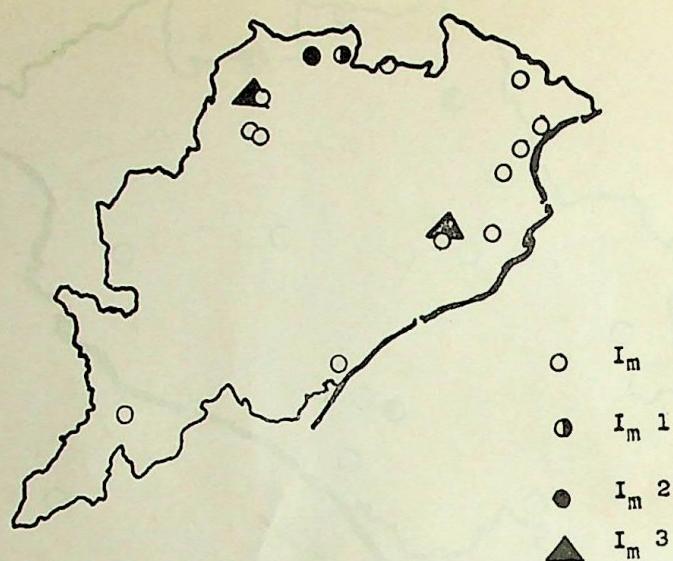


FIG. 6- Manufacturing Industry

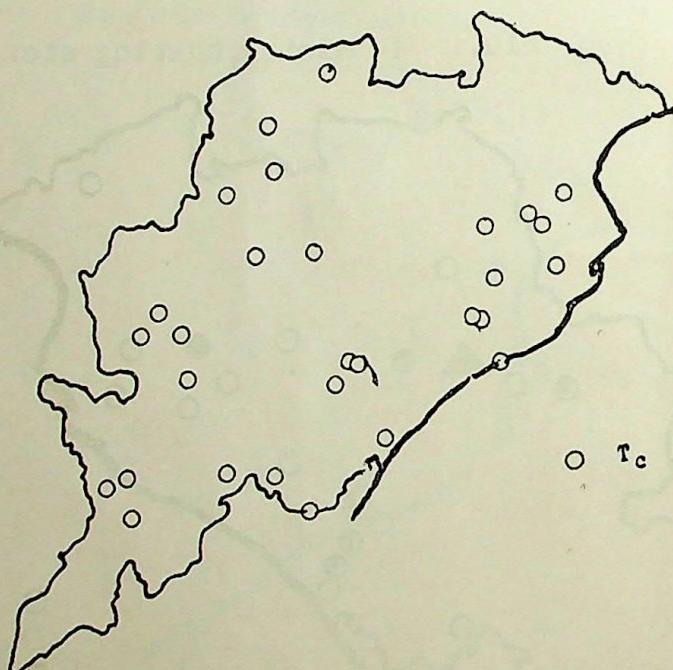


FIG. 7 Trade and commerce

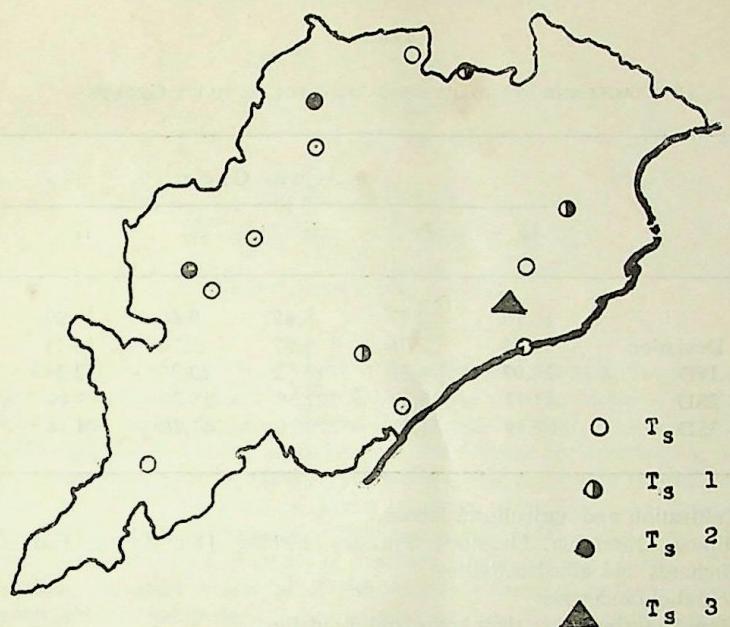


FIG. 8- Transport, storage &amp; communication

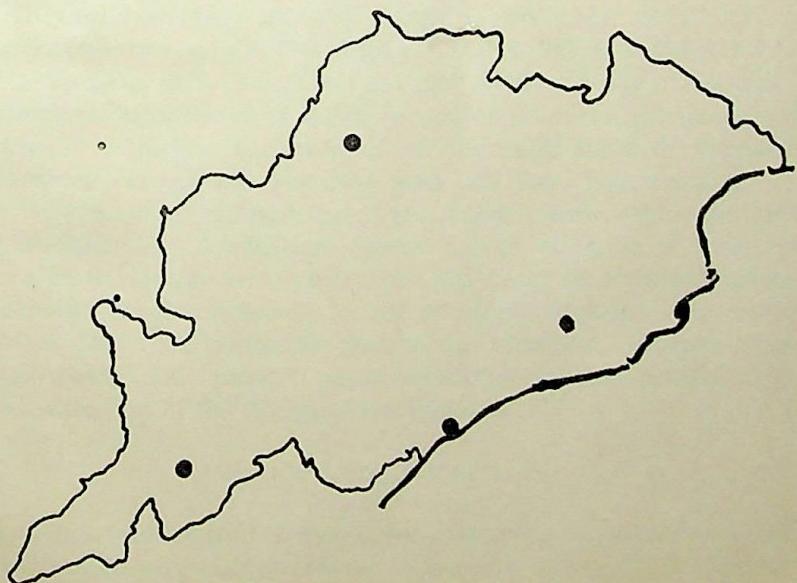


FIG. 9 Diversified

## APPENDIX

## TABLE

## AVERAGES AND STANDARD DEVIATIONS FOR ACTIVITY GROUPS

	Activity Groups					
	Ag	Pr	Ih	Im	Tc	Ts
Average	16.16	2.77	8.65	9.66	11.29	6.33
Standard Deviation	13.81	3.76	6.87	12.70	10.95	7.72
Average+ISD	29.97	6.53	15.52	22.36	22.24	14.05
Average+2SD	43.72	10.29	22.39	35.06	33.19	21.77
Average+3SD	67.59	14.05	29.26	47.76	44.14	29.49

*Ag*—Cultivation and agricultural labour.

*Pr*—Mining, Quarrying, Livestock, Forestry, Fishing, Hunting and Plantations, Orchards and allied activities.

*Ih*—Household industries.

*Im*—Manufacturing other than household industries.

*Tc*—Trade and Commerce.

*Ts*—Transport, storage and communications.

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## TECTONIC SIGNIFICANCE OF BOUDINAGE STRUCTURE IN GANGPUR METASEDIMENT

D. N. KANUNGO

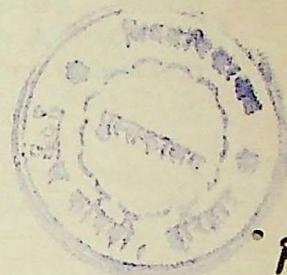
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Boudinage structure is observed in the competent lithologic horizons of Gangpur metasediments set in incompetent matrix. Such structures are seen both in the bedding layers as well as in the mineral veins that have later formed parallel to bedding or cleavage. The boudins are developed in the "a-tectonic direction" of the Gangpur fold belt perpendicular to the regional fold trend. They clearly indicate that the direction of fold axis in the Gangpur metasediments was a direction of stretching or tension which is supported from other evidences such as geometry of stretched pebbles and cross joints. The boudinage structure as also other deformatory structures in the Gangpur metasediments are believed to have been formed by a north-south directed compression and an east-west direction of stretching parallel to the fold axis.

### INTRODUCTION

BOUDINAGE structures are well known in deformed rocks and have been described by many authors such as CLOOS 1947, RAMBERG 1955, RAST 1956, COE 1959, WILSON 1961 and others. Study of boudins is of considerable significance as it provides information on the stress/strain orientation in the rocks. Such structures are primarily due to the differences in competency between the boudined layer and the adjacent rocks. The former behaves as a relatively more competent member than the latter during deformation. Boudins are formed due to extension of competent layers within the incompetent environment and hence are tensional features.

Boudinage structures parallel to the *b*-tectonic direction are reported more often than their occurrence parallel to *a*-tectonic direction in the deformed rocks. The present paper describes boudins parallel to the *a*-tectonic direction of the Gangpur Synclionorium.

### FIELD OBSERVATIONS

Boudinage structure is developed in the calcareous and arenaceous rocks of Birmitrapur Stage of Gangpur Series. It is mostly observed in the northern limb of the fold belt, while in the southern limb only a few examples

have been noted. Such structures are seen both in the bedding layers of the rocks as well as in the mineral veins that have later intruded into these formations. The thickness of boudins vary from a few centimetres to within one meter. A summarised statement of various aspects of boudinage is presented in the following table for reference.

TABLE 1—EXAMPLES OF BOUDINAGE STRUCTURE

Composition of boudin layer.	Composition of matrix	Boudin cross section.	Structural aspect of layer.	Reference to Figures.
Quartzite	Phyllite	Rectangular to barrel shape	Boudin layer parallel to bedding	Fig. 1a
Phyllitic Quartzite	Phyllite	-do-	-do-	Fig. 1b
Quartzite	Calc-Phyllite	-do-	-do-	Fig. 1c
Dolomite	Calc-Phyllite	-do-	-do-	Fig. 1d
Calcite Veins	Crystalline limestone	Lens shape	Boudin layer parallel to mineral veins	Fig. 2a
Calcite Veins	Dolomite	-do-	-do-	Fig. 2b
Quartz Veins	Crystalline Limestone	-do-	-do-	Fig. 2c

## BOUDINS IN BEDS

Figures 1a to 1d show a few examples of boudinage in beds. Figures 1a to 1c show boudinage in quartzite bands interbedded in phyllite or calc-phyllites. The boudins are barrel shaped or rectangular in cross-sectional shape. Their width is parallel to the strike of the bedding and regional fold axis and their elongation perpendicular to the fold axis. Hence they are oriented in the "a-tectonic direction" of the fold system. The separation of boudins is marked by mineralised extension fractures which are often represented by lens-shaped quartz veins. The phyllitic bands seem to flow into the gaps between the boudins. Figure 1d shows boudinage structure in dolomite bands interbedded in impure carbonate matrix.

**BOUDINS IN MINERAL VEINS**

Figures 2a to 2c show some examples of mineral veins that are boudinaged. These mineral veins are composed of either quartz or calcite and are generally emplaced parallel to local bedding or cleavage planes in rocks. They have been stretched parallel to their strike and boudins are formed along their dip direction which is here perpendicular to the local fold axis.

Figures 2a and 2b show boudinage in calcite veins set either in crystalline limestones or in dolomites and figure 2c shows boudinage structure in quartz vein set in crystalline limestones.

The boudins of the mineralised veins are generally lens-shaped in cross section. Their thickness varies depending on the thickness of the original mineral veins which is usually within 10 cm.

From the above field observation two aspects are noted about the boudinage structure in Gangpur metasediments (i) the geometry of cross section of the boudins and (ii) elongation of the boudins.

(i) The cross sections of boudins are either lens, barrel or rectangular shaped. Boudins of quartzite layers in a phyllite matrix show rectangular to barrel shaped cross-sections. Boudinaged calcite veins in dolomites and limestones have a lens-shaped cross section (see Table above). It appears from the foregoing evidence that the cross sectional structures of boudins is a function of the difference between the relative competencies of the layer that is being boudined and the matrix (RAMBERG 1955).

(ii) The elongation of the boudins, wherever observed in the field, run up and down the layer that is boudined and is parallel to the local dip of the bedding surfaces. Since bedding, in general dips either to the north or to the south in the Gangpur fold belt, the boudins also plunge northwards or southwards. As the regional fold axis trends east-west the long dimension of boudins are at right angles to the trend of the fold axis. Hence the boudins occur parallel to the "a-tectonic direction" of the Gangpur fold belt. In geologic literature boudinage structures reported by early workers, such as, CLOOS 1947, RAMBERG 1955, RAST 1956 and WILSON 1961, are described by them as oriented parallel to the fold axis (*b*-tectonic direction) of the rocks. The present example is rather unusual in this respect. COE 1959 has reported a similar example in West Cork, Ireland.

**DYNAMIC SIGNIFICANCE OF THE BOUDINAGE STRUCTURE**

Study of boudins is of considerable significance as they provide information on the stress/strain orientations in the rocks. In the present case the direction of stretching or tension as revealed by the boudin geometry is east-

west, i. e., parallel to the fold axis of the region and the direction of maximum compressive stress is north-south.

The extension fractures associated with the boudins, now represented by flat, lenticular quartz veins, can also be used for determining the stress/strain axis in the rocks. A line perpendicular to the extension-fracture is parallel to the width of the boudin and this in turn is the direction of stretching in the rocks. The line of intersection of boudinaged layers and the plane of the extension-fracture is parallel to the length of the boudins which gives the direction of *P*-intermediate stress. The plane of the extension-fracture contains the direction of maximum compressive stress (*P*-maximum) and this direction is perpendicular to the elongation of boudins (WILSON 1961). From the geometry of extension-fracture it is known that the direction of stretching is east-west parallel to the fold axis and the maximum compressive stress is directed north-south.

The geometry of deformed pebbles and cross joints in the Gangpur metasediments also point to the same observation, i. e., the direction of stretching is east-west parallel to the fold axis and the maximum compression was in a north-south direction.

Thus it is concluded that the boudins as also other deformatory structures in the Gangpur metasediments were formed by a north-south maximum compressive stress and an east-west direction of stretching parallel to the fold axis. This supports the thesis advanced by RAMSAY (1967, P.112-113). According to Ramsay "the strain ellipses have one principal extension and one principal contraction. This arrangement produces folding in one direction and boudinage or cross jointing perpendicular to the lines of fold axis." This type of deformation involving a principal direction of elongation parallel to the fold axis has been stated by many authors (Ref. OELE 1966, P.133, table 1).

#### CONCLUSION

The boudinage structure in Gangpur metasediments are observed parallel to the "a-tectonic direction" of the Gangpur fold belt which is a rare occurrence. It is inferred that these structures as well as other deformatory structures in the Gangpur metasediments were formed by a north-south maximum compressive stress and an east-west direction of elongation parallel to the fold axis.

#### ACKNOWLEDGEMENT

One of the authors (N. K. Mahalik) is grateful to the Sambalpur University for the research grant awarded to him to complete the Research Project of which the present forms a part.

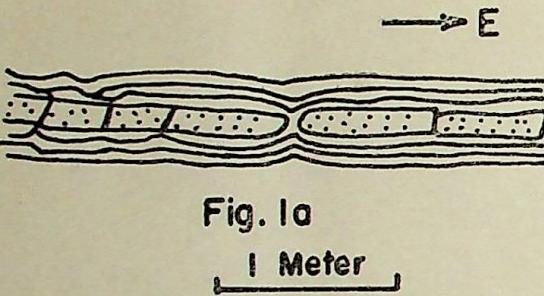


Fig. 1a

1 Meter

Boudined quartzite band  
in Phyllite on Khatma  
nalla bed south of Pandua.

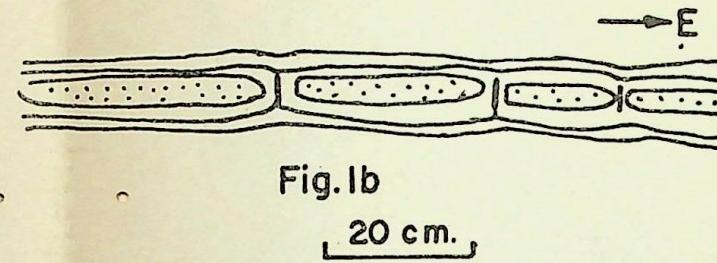
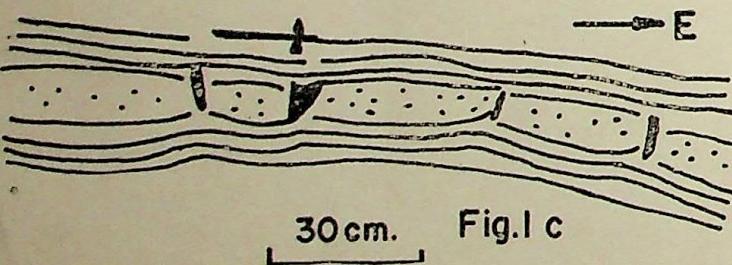


Fig. 1b

20 cm.

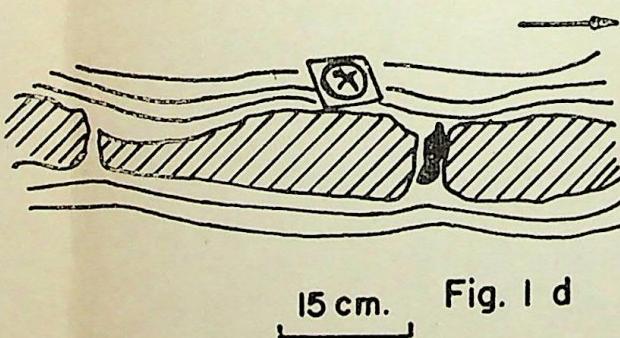
Boudined Phyllitic quartzite band  
in Phyllite on Khatma Nalla bed  
south of Pandua.



30 cm.

Fig. 1 c

Boudined quartzite band in  
Cal-careous Phyllite on Khatma  
Nalla bed north of Kandarkela.



15 cm.

Boudined Dolomite band in Calcareous  
Phyllite at Jagda Quarry.

#### BOUDINAGE IN BEDDING UNITS

Fig. 1

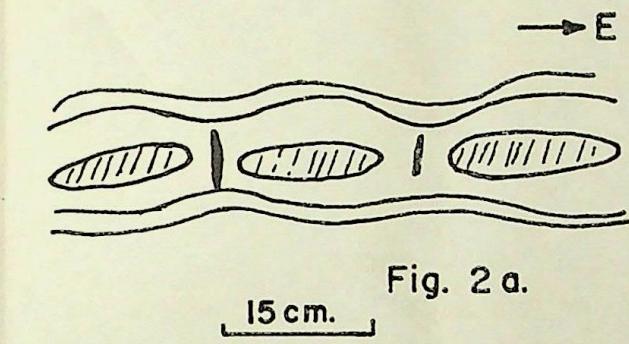


Fig. 2 a.

Boudined Calcite vein in  
crystalline limestone at  
Purunapani limestone quarry.

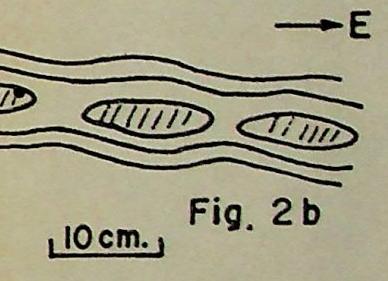
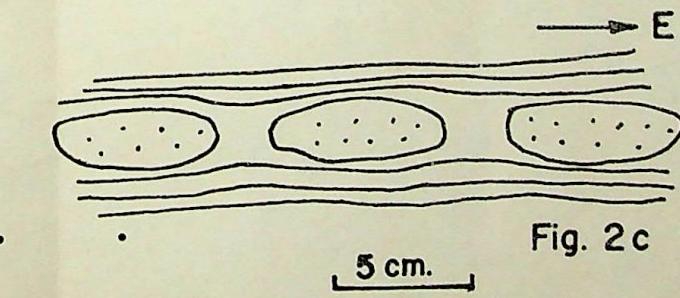


Fig. 2 b

Boudined Pink Calcite vein in  
Dolomite on Khatma Nalla  
bed south of Pandua village.

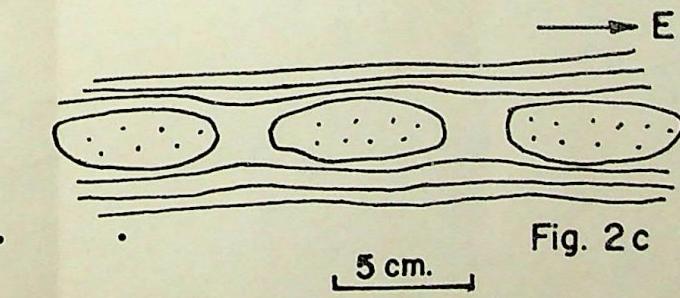


Fig. 2 c

Boudined quartz vein in  
crystalline limestone on  
Khatma Nalla south of Bhojpur.

#### BOUDINAGE IN MINERAL VEINS

Fig. 2

# METAMORPHISM IN THE EASTERN PART OF GANGPUR SERIES

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Metamorphism in the eastern part of Gangpur Series and its relation to stratigraphy, structure, tectonics and granitic intrusion have been discussed. Three phases of metamorphic recrystallisation are observed. The early low grade metamorphic phase ( $M_1$ ) belonging to the green schist facies is related to the main movement phase ( $F_1$ ) which deformed the Gangpur Series into a major synclinorium. The early phase was followed by the main phase of metamorphism ( $M_2$ ) belonging to the lower amphibolite facies. This phase represents the highest grade of metamorphism for this area. This phase is mainly post-tectonic in relation to the main movement phase ( $F_1$ ). It is believed to be a result of granitic intrusion into the adjoining area and has no relation to depth of burial or tectonic level. The progressive metamorphism of the early and main phase was followed by a late phase retrograde metamorphism ( $M_3$ ) belonging to the green-schist facies.

## INTRODUCTION

A N attempt has been made to present certain aspects of metamorphism in the eastern part of Gangpur Series. More than 500 square km. have been covered which constitute nearly a third of the total extension of Gangpur Series. The area was mapped on 2" to a mile scale. About 400 thin sections were studied.

There is no systematic published work on metamorphism of these rocks. The most extensive study of the whole of Gangpur Series was made by M. S. KRISHNAN (1937) where he has given certain broad generalisation about metamorphism.

## STRATIGRAPHY

In the discussion of metamorphism it will be useful to give the stratigraphic sequence and lithologic contents. A variety of sedimentary rocks with associated basic dykes and sills, in various stages of metamorphism, constitute the Gangpur Series. Their detail stratigraphy is shown in table I. The revised stratigraphy after KANUNGO and MAHALIK (1967 ; 1970) is presented here. This is just the reverse of the one proposed by KRISHNAN 1937. The Gangpur Series lies unconformably over the Iron-

ore Series rocks and begins with a basal conglomerate horizon of Raghunathpalli stage. The Raghunathpalli stage is successively followed upwards by Laingar, Birmitrapur, Kumarmunda and Ghoriajor stages. They are intruded by basic dykes and sills followed by granite intrusion. The granites are not exposed in the present area of investigation but lie very close to it towards the north and north-west (Fig. 1). The granite intrusives are associated with numerous quartz and tourmaline veins which are found in the present area.

TABLE I.—STRATIGRAPHY OF GANGPUR SERIES (After Kanungo and Mahalik 1967)

		Granites and associated quartz, tourmaline veins. Metabasic dykes and sills (epidiorite, amphibolite).
GANGPUR SERIES	<i>Ghoriajor Stage :</i>	Staurolite and Garnetiferous mica schist, epidote mica-schist, chlorite schist, quartzites and conglomerates.
	<i>Kumarmunda Stage :</i>	Staurolite bearing carbonaceous phyllites, spotted carbonaceous phyllites, Carbonaceous slates, Banded Carbonaceous quartzite.
	<i>Birmitrapur Stage :</i>	Crystalline Limestone, Dolomites, tremolite schists, interbedded quartzites, phyllites and Calc-phyllites.
	<i>Laingar Stage :</i>	Argillaceous phyllites, staurolite and garnetiferous schist, fine grained quartzites, carbonaceous slates and phyllites, phlogopite-tremolite-carbonate rocks.
	<i>Raghunathpalli Stage :</i>	Conglomerate, quartzites, quartz schist, slate.

## UNCONFORMITY

IRON-ORE SERIES	Slate, Phyllite, Staurolite-garnet schist, Calc-gneisses.
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## STRUCTURE AND TECTONICS

From the analysis of mesoscopic structures and stratigraphic sequence it is observed that the rocks have been folded into a major east-west synclinorium structure. The structure closes to the east. There are many large scale folds in the different lithologic horizons in the synclinorium. The plunges of the fold axes vary in their orientation in different localities. In the southern limb the fold axes regularly plunge at low angles in the west-south-westerly direction, in the northern limb it plunges either to east or west and in the western portion of the present area the folds regularly plunge to the east. The south limb of the synclinorium is inverted and overturned to the north while the northern limb is either normal, dipping to south at steep angles or inverted with northerly dips. Inverted northerly dips are well observed in the Birmitrapur area. Thus in some sections both the limbs of the synclinorium are inverted.

A number of major faults (wrench type) and shear zones are associated with the synclinorium.

A wide variety of secondary mesoscopic structural features are present in the rocks which give an idea of the nature and sequence of deformation in the rocks. There was a main phase of movement ( $F_1$ ) which deformed the rocks into the synclinorium structure. During this phase a variety of cleavages and lineations were formed. Some of the cleavages are due to preferred mineral growth either parallel to axial plane of folds ( $S_2$ ) or oblique to the axial plane ( $S_3$ ) and referred to here as slaty cleavage where as others are mechanical fractures either parallel to or oblique to axial plane of folds and referred to here as fracture cleavage. After the main fold movement ( $F_1$ ) the pre-existing micaceous foliations have been crenulated and a crenulation cleavage ( $S_4$ ) and lineation ( $L_2$ ) are observed in the schistose, phyllitic and slaty rocks. The orientation of the crenulation lineation is controlled by the orientation of the pre-existing planes on which they are observed. They have a low easterly plunge and make various angles with the early lineation ( $L_1$ ). The early linear structure is not sufficiently deformed by the late crenulation movement. There is no new mineral growth marking the crenulation cleavage.

At various stages during the deformation, the competent horizons like quartzites, dolomites have undergone brittle rupture and have given rise to a number of shear and tension fractures.

It seems probable that the emplacement of granite took place subsequent to the main folding of the rocks.

#### METAMORPHISM

##### *Zones of metamorphism :*

The zones of metamorphism were marked by mapping the first appearance of certain index minerals such as biotite, garnet, etc., in pelitic sediments. Isograds of biotite, garnet and staurolite are shown in the present area (Fig. 1). From the distribution of zones it is seen that there is a progressive spatial variation in the degree of metamorphism. The grade of metamorphism rises to the north and north-west. In the map (Fig. 1) the biotite zone is not significantly observed. It has a limited occurrence. More often the biotite and garnet isograds merge together, thus sometimes, the garnet zone appears after chlorite zone and the biotite zone is skipped over. The staurolite zone is also not a prominent zone. It has a patchy distribution inside the garnet zone. It is probably confined to lithologically suitable horizons.

There is some amount of difficulty in plotting the zones of metamorphism for the entire exposures of Gangpur metasediments since it consists of several lithologic types. One uniform composition is lacking for the whole area. The present mapping of the isograds is done with respect to available pelitic

horizons in some stages. Isograd mapping for calcareous rocks of Birmitrapur stage and carbonaceous rocks of Kumarmunda stage is difficult.

The metamorphosed products are classified mainly into two grades : those south of garnet isograd belong to a low grade (green-schist facies) and those north of garnet isograd are medium grade (amphibolite facies). The boundary between the two groups of rocks is shown in the map. The facies names are after TURNER (1968).

The low grade zone is characterised by sericite, quartz, chlorite, calcite, dolomite, epidote, albite, and rarely biotite mineral assemblages and the middle grade zone by muscovite, biotite, phlogopite, tremolite, hornblende, plagioclase, garnet, staurolite, calcite, quartz mineral assemblages. Kynite and sillimanite are not developed in the area.

In the south and eastern part of the area the rocks are generally conglomerate, quartzite, slate, phyllite, limestone, dolomite, carbonaceous slates and epidiorites belonging to the green-schist facies, whereas to the north and north-west the rocks are garnet and staurolite bearing schists calc-schists, crystalline limestones, marble, amphibolite and biotite gneiss belonging to the amphibolite facies. The lithology and mineral composition of each stratigraphic unit varies in the two principal metamorphic zones which is shown in the table II.

#### *Phases of metamorphism :*

Most of the pelitic rocks show the following characters under the microscope.

1. The secondary foliation ( $S_2$ ) is made up of a parallel orientation of flaky or flattened minerals, such as sericite, chlorite, muscovite, biotite and quartz. They represent the early foliation related to the main fold movement.
2. Porphyroblastic minerals of biotite, garnet, staurolite have grown mostly subsequent to the formation of the early foliation since they deform the foliation and contain inclusion patterns  $S_i$  supposed to be equivalents of this foliation (Photograph 1).
3. (i) The porphyroblasts have later changed to low grade minerals, e. g., garnet and biotite to chlorite ; staurolite to an aggregate of sericite and quartz.
3. (ii) Large plates of chlorite have developed across the foliation containing inclusion patterns which are mineralogically and texturally similar to the external patterns. The  $S_i$  pattern in these chlorites (Photograph 2) are much coarser than the  $S_i$  pattern observed in the early porphyroblasts of garnet, biotite etc.

From the above observations we can conclude that there are three distinct phases of mineral formation under the varying metamorphic conditions prevailing.

TABLE II.—LITHOLOGICAL CHARACTER OF ROCKS OF GANGJUR SERIES IN DIFFERENT METAMORPHIC ZONES

Formation.	Lithology in the low grade zone, South and eastern part of the area.	Lithology in the middle grade North-western part of the area.
Raghunathpalli stage.	<i>Rocks</i> : slates, phyllites, sericite-quartz schist, quartzite, conglomerate.  <i>Minerals</i> : sericite, quartz, iron-ore, chlorite, biotite tourmaline.	Conglomerate, muscovite-quartz schist, biotite gneiss.  muscovite, biotite, microcline oligoclase, quartz, garnet.
Laingar stage.	<i>Rocks</i> : phyllite, carbonaceous-slates, quartzite.  <i>Minerals</i> : quartz, sericite, chlorite,	Garnetiferous schist, tremolite schist.  muscovite, biotite, garnet, staurolite, tremolite, calcite, quartz, phlogopite, chlorite (retrograde origin).
Birmitrapur stage.	<i>Rocks</i> : limestone, dolomite quartzite, phyllite.  <i>Minerals</i> : sericite, quartz, calcite, dolomite, microcline.	crystalline limestone, calcareous schist.  calcite, quartz, tremolite, phlogopite.
Kumarmunda stage.	<i>Rocks</i> : carbonaceous-slates, phyllite, banded carb-quartzite.  <i>Minerals</i> : quartz and carbonaceous matter.	Staurolite bearing schists and phyllites, knotted or spotted carbon-phyllite, banded carbonaceous quartzite.  Biotite, garnet, staurolite, quartz, carbonaceous matter, chlorite (retrograde origin).
Ghoraijor stage.	<i>Rocks</i> : no equivalent.  <i>Minerals</i> :	mica-schist, epidote-schist, muscovite, biotite, garnet, staurolite, chlorite (both-relict and retrograde), epidote, hornblende and plagioclase.
Intrusive basic igneous rocks.	<i>Rocks</i> : epidiorite, green-schist.  <i>Minerals</i> : epidote, actinolite, albite, quartz, chlorite.	Amphibolite, greenish blue hornblende, plagioclase, garnet.

*Relation to structure and stratigraphy :*

From the map (Fig. 1) showing the distribution of metamorphic zones in Gangpur Series it is observed that grade of metamorphism is not accountable to the stratigraphic level or tectonic position in the synclinorium. Rocks of all horizons lying in the northern limb and the centre of the synclinorium are uniformly metamorphosed to a staurolite grade whereas similar rocks lying on the southern limb of the synclinorium are only metamorphosed to a chlorite grade.

*Relation to deformation phases :*

Petrographic study of relation of minerals to mesoscopic structures and the internal patterns ( $S_i$ ) in the porphyroblasts have been utilised for correlation of metamorphism with the deformation phases.

Ground-mass minerals like sericite, chlorite, muscovite, biotite and garnet recrystallised first and their preferred orientation define the early foliation related to the main fold movement ( $F_1$ ). This is the first phase of recrystallisation ( $M_1$ ) formed during ( $F_1$ ) movement.

Porphyroblasts like biotite, garnet, staurolite, chlorite and rounded knots in carbonaceous rocks grew subsequently and present the following relation to deformation movement which is decipherable from their preserved internal patterns ( $S_i$ ). Such  $S_i$ -patterns in porphyroblasts and their relation to their external planar pattern ( $S_e$ ) have been extensively utilised for correlation of movement phases with metamorphic mineralisation (JOHNSON 1963, ZWART 1963, TURNER and WEISS 1963).

*Biotite porphyroblasts :*

Biotite porphyroblasts are well developed in the pelitic rocks of Ghoriajor stage toward the centre of the synclinorium. A variety of biotite porphyroblasts are observed which differ in their pleochroic scheme. The pale yellow to dark green variety is very common, although colorless to dark brown variety is also present. In greenish phyllites a deep orange variety is also observed. Some of the biotite porphyroblasts are rod like, sometimes oriented in the schistose surface to produce a mineral lineation parallel to the pucker lineation ( $L_2$ ). Under the microscope these biotite porphyroblasts have a distinct lensoid shape (Photograph 1). The (-001) cleavage of biotite porphyroblasts have no regularity of orientation. It may make any angle with the foliation as well as with the elongation of the biotite grains.

Biotite often shows an internal inclusion pattern ( $S_i$ ) consisting of fine grains of quartz and iron ore (Photograph 1). Their texture is fine compared to the coarse external foliation. The inclusion pattern is straight and at an angle to the external pattern ( $S_e$ ). These internal features show that biotite grew post-tectonically to the main movement phase and the angle between  $S_i-S_e$  shows a relative post-crystalline rotation of the porphyroblasts. The lensoid porphyroblasts showing planar internal patterns are very much

similar to those shown in figure 8 of ZWART (1962). The obliquity of  $S_i$ - $S_e$  relation according to ZWART is a result of rotation of porphyroblasts. However, it is doubtful if such elongate porphyroblasts can rotate across the foliation. It is probable that the ground-mass was flattened around the porphyroblasts showing a relative rotation (RAMSAY 1962). Some of the elongate biotite porphyroblasts might have got reoriented in the direction of pucker lineation during crenulation movement ( $F_2$ ). The crenulation cleavage ( $S_4$ ) curves around the biotite porphyroblasts indicating the earlier presence of porphyroblasts.

Indication of biotite forming earlier than the garnet porphyroblasts are not available but they show evidence that they formed simultaneously. The texture and angular relation of  $S_i$ -patterns to  $S_e$ -patterns in both biotite and garnet in a particular slide is similar. In rare cases biotites enclose euhedral garnet indicating formation of biotite later to garnet.

#### *Garnet porphyroblasts :*

Garnet porphyroblasts are well developed in the pelitic schists of Laingar and Ghoriajor stages and the carbonaceous rocks of Kumarmunda stage occurring in the medium grade metamorphic zone.

The garnets show straight  $S_i$ -patterns at an angle to  $S_e$ -pattern indicating post-tectonic silent crystallisation. However, these garnets are formed prior to the crenulation movement ( $F_2$ ) since the crenulation cleavage curves round the rigid porphyroblasts. During this crenulation movement ( $F_2$ ) there is a relative movement between porphyroblast and ground-mass giving rise to the  $S_i$ - $S_e$  angularity.

Garnets must have formed in two stages since some garnets show a turbid central zone rimmed by a clear zone. Some idioblastic garnets are found included in staurolites indicating the early formation of garnets.

#### *Staurolite porphyroblasts :*

It occurs in the medium grade rocks in the centre of the synclinorium and in the north limb in pelitic schists and carbonaceous phyllites. Staurolites formed in a post-tectonic phase since they contain straight  $S_i$  patterns. They were formed subsequent to the garnets as they contain garnet idioblasts as inclusion in them.

#### *Incipiently recrystallised knots in carbonaceous phyllites :*

These rounded knots are observed in the carbonaceous phyllites of Kumarmunda stage occurring in hills south of Purunapani at Ranakata. These knots are embedded in fine grained matrix. They show an internal pattern  $S_i$  which is straight for most part, but slightly sigmoidal at the margin. This shows that the knots were formed under static condition after the main movement phase ( $F_1$ ) but towards their final development they were affected by crenulation movement.

*Chlorite :*

Well developed plates of chlorite grew at the close of the deformation history. They contain  $S_i$ -patterns which are similar to the external pattern ( $S_e$ ) in their texture and orientation (Photograph 2). The textural similarity indicates that the chlorites were formed after the schistosity attained its final state. Some of the chlorites are pseudomorphs after biotite and garnet porphyroblasts.

*Quartz :*

Porphyroblastic quartz occurs in the pressure shadows around biotite and garnet porphyroblasts and also along shear and tension fractures affecting brittle rocks.

*Iron-ore :*

Besides the fine grained iron-ore present in the ground-mass porphyroblastic iron-ores (magnetite) is found in the carbonaceous phyllites in the centre of the synclinorium. The magnetite porphyroblasts are associated with staurolite porphyroblasts and form a mineral lineation.

*Conclusion about recrystallisation of minerals :*

From the above study we may conclude that although recrystallisation of ground-mass minerals began during the main folding the mineralisation of a higher grade of metamorphism took place mainly in the post-tectonic phase prior to the crenulation movement ( $F_2$ ) and continued further beyond. The metamorphism during these phases were progressive in nature. The crystallisation of biotite, garnet, staurolite represent the peak of progressive metamorphism. Towards the final phase retrograde condition prevailed when low grade minerals formed.

There is no direct evidence to suggest that the retrograde process is related to any special structural feature or movement. The retrogression may be due to general lowering of metamorphic conditions.

*Relation to granite intrusion :*

A glance at the geologic map will show that the high grade metamorphic rocks are associated in space with granites. It is a good indication that the intrusion of granite towards close of main folding provided the necessary heat for metamorphism.

*Causes of metamorphism :*

From the metamorphic map it is seen that there is a progressive increase of metamorphic condition in space. There is also a causal connection between the high grade metamorphic rocks and granite intrusion. Although addition of heat from granite intrusion was the cause of progressive increase in the intensity of metamorphism towards north-west, high temperature

was not the only essential physical condition for recyrstallisation. Non-uniform stress due to horizontal compression was an important factor for controlling the character of the resulting rocks which are different from those produced by heat alone. Load is not an important factor in this area since stratigraphically and tectonically higher levels are more metamorphosed. Whereas the igneous intrusion was responsible for higher grade of metamorphism the low grade rocks are definitely the result of fold movement.

The chronological relation between orogeny, granite intrusion and metamorphism is shown in table III.

TABLE III.—CHRONOLOGICAL RELATION BETWEEN OROGENY GRANITE INTRUSION AND METAMORPHISM

Orogeny	Granite Intrusion	Metamorphism
Crenulation movement ( $F_2$ )	Granite intrusion. $M_2$ :	$M_3$ : Retrograde metamorphism. Development of chlorite porphyroblasts either neocrystallised or as pseudomorphs after biotite and garnet.
Main fold movement ( $F_1$ ).		$M_2$ : Metamorphism belonging to the lower amphibolite facies. Development of porphyroblasts of biotite, garnet and staurolite.
		$M_1$ : Metamorphism belonging to the green schist facies. Development of sericite, chlorite & biotite which make the early foliation related to the main folding.

#### *Equilibrium condition during metamorphism :*

Some mineral associations such as chlorite, garnet and staurolite in the rocks suggest that the rocks have not attained chemical equilibrium during metamorphism. The chlorite is of two generations, one is found as a relict mineral not affected during progressive metamorphism and the other is a retrograde product. During retrogression some of the high grade minerals have partly altered while others have not been affected at all. Thus in the same rock, conditions of both progressive disequilibrium and retrogressive disequilibrium are observed (BILLINGS 1937, NAHA 1965).

#### *Metamorphism in Iron-Ore Series :*

No attempt has been made to study metamorphism of adjoining Iron-Ore Series in any great detail. However a few observed facts collected during

reconnaissance can be mentioned here. The enclosed map shows the zones of metamorphism in the rocks of Iron-Ore Series south of Gangpur Series. There is a progressive spatial variation of grade of metamorphism in these rocks. It increases to the south. The highest grade of rocks belong to the amphibolite facies (staurolite grade). They show evidence of retrogression after the high grade metamorphism. To the north of Gangpur Series the rocks of Iron-Ore Series are uniformly metamorphosed to garnet grade. It is difficult to correlate metamorphism in Iron-Ore Series with that of Gangpur Series.

#### CONCLUSION

The metamorphic minerals in the eastern part of Gangpur Series were produced in three successive phases. The early phase belonging to the green-schist facies was produced during the main period of fold movement. The second phase of metamorphism belonging to the lower amphibolite facies was produced after the main fold movement as a result of granite intrusion into the adjoining area. This represents the peak of progressive metamorphism, in Gangpur Series. This has no relation to the stratigraphic and tectonic levels. The third and final phase is of retrograde nature. Although igneous intrusion was responsible for higher grade metamorphism the low grade rocks are the result of folding only.

#### ACKNOWLEDGEMENTS

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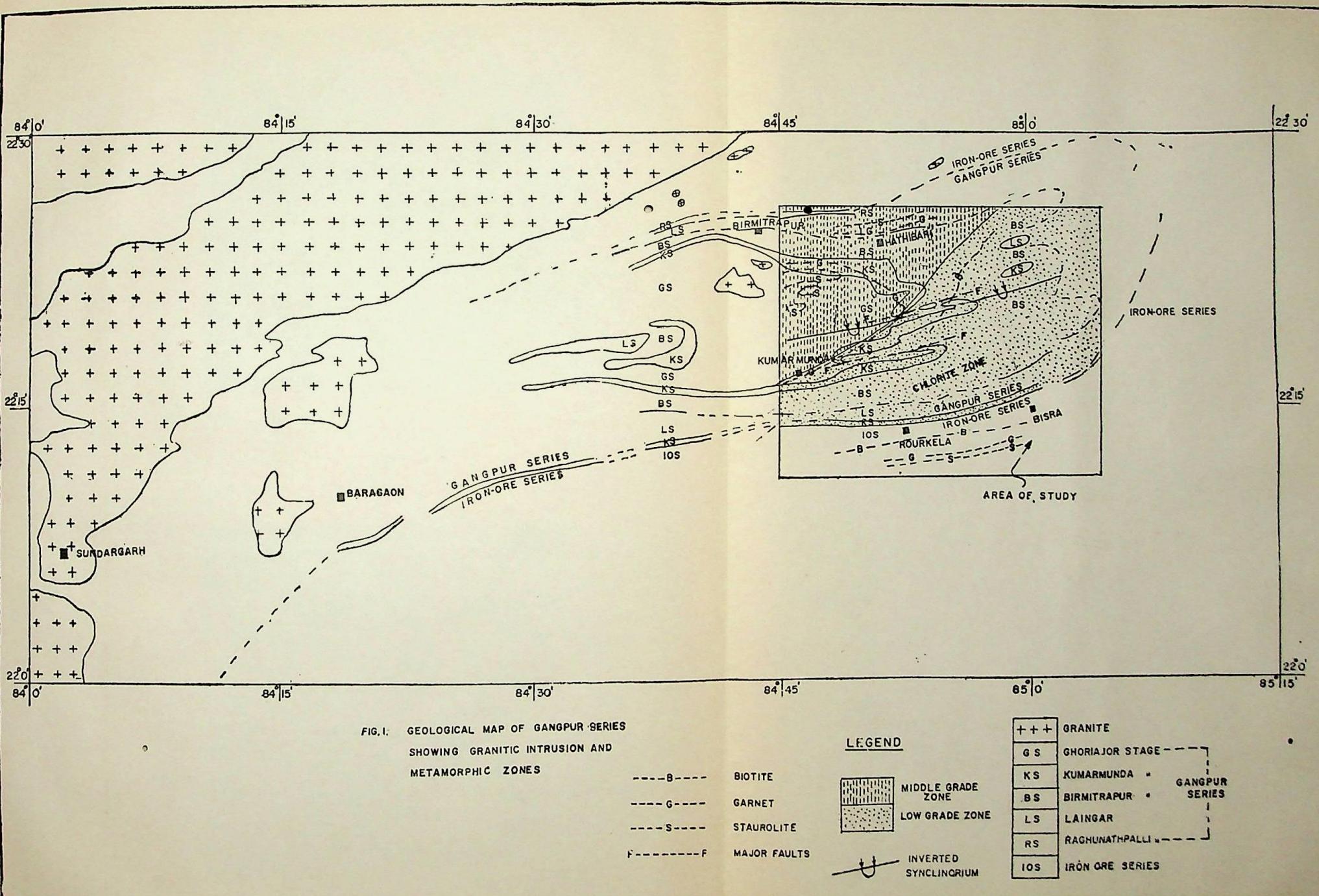
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**Explanation to illustrations :**

Fig. 1. Geological map of Gangpur Series showing granite intrusion and grade of metamorphism.

Photograph—1. Biotite porphyroblast from the centre of Gangpur Synclinorium.

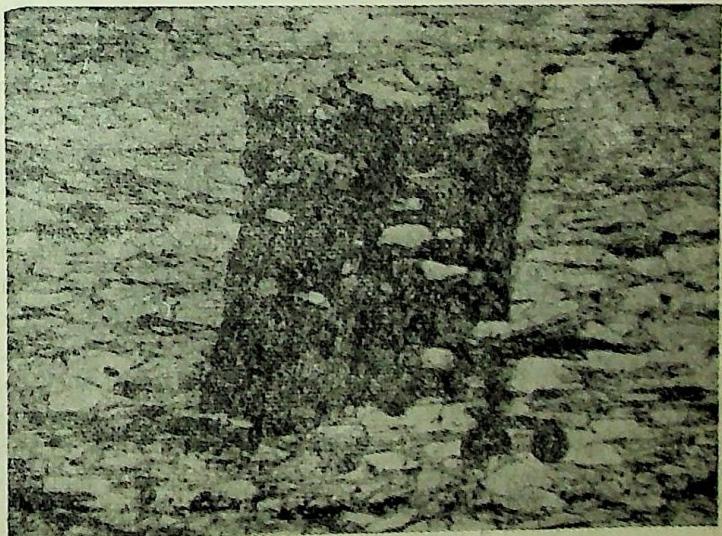
Photograph—2. Chlorite porphyroblast from centre of Gangpur Synclinorium.







Photograph—1. Biotite Porphyroblast from the centre of Gangpur Synclinorium.



Photograph—2. Chlorite Porphyroblast from the centre of Gangpur Synclinorium.

‘ON DISLOCATION MECHANICS ASSOCIATED WITH EXPLOSIVE  
FORMING OF METALS’

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This paper is an attempt at bringing out the necessity of viewing the deformation process under explosive loading conditions from the metallurgical point of view. The significant influence of dislocation mechanism, under the unconventional loading, high strain rates and temperatures encountered in explosive forming, on material formability parameters like flow stress, work-hardening, ductility etc., is surveyed.

#### 1. 0. INTRODUCTION

THE high energy rate forming processes (HERF), of which explosive under-water stand-off operations form a distinct class, have come to the rescue of modern manufacturing requirements. These are mainly centered round low-cost development of the production of components from high strength alloys. This has been necessitated by the space science developments. The ease with which metals, difficult to form otherwise, have been formed to close tolerances without appreciable variation of terminal properties by the HERF processes, was little understood in the early stages of development of the process. The increase in ductility and higher flow stress without fracture had led to an anticipation of the disappearance of many awkward conventional forming processes. Most of such optimism has now turned out to be unjustified, but it is still widely acknowledged that HERF processes have got their own advantages and their field of application starts mostly where conventional processes have no technical and economical answers to production. But the main drawbacks and advantages can be fully realised only when a concerted effort is made by the workers in the field to study the process from production, material behaviour and metallurgical points of view.

## 2.0. FORMABILITY AND DISLOCATION MECHANISMS

For under-water stand-off explosive forming operations, the formability criteria have been functionally co-related by Ezra<sup>1</sup> in the following parametric equation :—

$$F \left[ \frac{W}{D}, \frac{D}{t}, \frac{B}{D}, \frac{\sigma\gamma}{E}, \epsilon, \frac{\rho(\nu, \theta)}{\sigma\gamma}, \frac{f\mu}{\sigma\gamma D^2} \right] = 0$$

where 'W' is the maximum depth of draw, 'D' is the diameter of die opening, 'B' is the blank width, ' $\sigma\gamma$ ' is the static yield stress 't' is the blank thickness,  $\epsilon$  is the total elongation of blank material,  $\rho(\nu, \theta)$  is the explosive pressure on blank surface, 'S' is the stand off distance, 'f' is the hold-down force, ' $\mu$ ' is the coefficient of friction between the blank and its restraints, ( $\nu$  &  $\theta$ ) are the polar coordinates of any generic point with the center of blank as the origin and 'E' is the Young's Modulus of elasticity of blank material.

2.1. It is evident therefore that the system parameters have a far greater degree of influence on formability than the material properties. Nevertheless, the fact that the blank deforms plastically, strongly motivates a study of the kinetics of dislocation in the research on deformation criteria. The nature of loading and the impulsive action thereof makes analysis difficult since inertia forces on dislocations play by themselves, a major role. A picture of the dynamic loading regimes due to Lindholm<sup>2</sup> (Table 1) explains the mechanisms which lead to time-dependence in the constitutive equations

TABLE 1—DYNAMIC LOADING REGIMES (after Lindholm<sup>2</sup>)

	Usual Strain rate in $\text{Sec.}^{-1}$	Method of Loading	Dynamic consider- ations in Testing	
$10^8$ —	Hyper Velocity impact	Light gasgun or Explosive driven Projectile	SHOCK WAVE PROPAGATION.	
$10^7$ —				
$10^6$ —				
$10^5$ —				
$10^4$ —				
$10^3$ —	Impact	Mechanical or Explosive impact.	ELASTIC-PLASTIC WAVE PROPAGATION.	
$10^2$ —				
$10^1$ —				
0 —	Dynamic	Fast acting hydraulic or pneumatic machine.	MECHANICAL RESONANCE IN SPECIMEN AND M/C.	INERTIA FORCES IMPORTANT
$10^{-1}$ —				
$10^{-2}$ —				
$10^{-3}$ —	Static	Hydraulic or screw machine.	CONSTANT STRAIN RATE TEST.	
$10^{-4}$ —				
$10^{-5}$ —				
$10^{-6}$ —	Creep	Constant load or stress machine.	STRAIN VS. TIME OR CREEP RATE RECORDED.	INERTIA FORCES NEGLECTED
$10^{-7}$ —				
$10^{-8}$ —				

for plastically deforming bodies. Though the inertia forces are included in the equations of motion of deforming bodies or their dynamic equilibrium equations, they do not come into the constitutive equations which are basically the same for high and low rates of loading. Adequate experimental reports on the effects of explosive deformation on such macroscopic properties as ductility, yield strength, hardness etc., are available but little headway has been made in the study of dislocations under such extremely impulsive and differential loading conditions as are invariably associated with the explosive forming process.

**2.2.** In explosive forming operations the pressures and strain rates are of the order of 20 Kilobars and  $10^2$  per second respectively. The following material has been surveyed keeping this in view. It is evident from available experimental data that there exists a certain interdependence between rate and temperature sensitivities of the flow stress for which a constitutive equation of the type  $F(\sigma, \epsilon, \dot{\epsilon}, T)=0$  is needed. .... (1)

Reviewing the work of Dorn, Lindholm<sup>2</sup> gives the average rate of strain by an Arrhenius type equation,

$$\dot{\epsilon} = \dot{\epsilon}_o \exp\left(-\frac{H}{\kappa T}\right) \quad \dots \dots \quad (2)$$

based on the theory of thermally activated dislocation mechanism where ' $\dot{\epsilon}_o$ ' is a frequency factor, 'H' the energy that must be supplied by a thermal fluctuation to overcome the obstacles to dislocation motion in crystal structures 'k' the Boltzmann constant and 'T' is the absolute temperature. The energy 'H' is predominantly a function of stress ' $\sigma$ ' and is expanded in the form  $H=H(\sigma)$  in a Taylor series about  $\sigma^*$  where  $\sigma^*$  is the magnitude of the long range internal stress field opposing dislocation motion, an athermal component. Thus

$$H(\sigma) = H(\sigma^*) + \frac{dH}{d\sigma} (\sigma^*) [\sigma - \sigma^*] + \frac{1}{2} \frac{d^2H}{d\sigma^2} (\sigma^*) [\sigma - \sigma^*]^2 + \dots \dots \quad (3)$$

Retaining only the linear terms, we get

$$H(\sigma) = H_o - v^* (\sigma - \sigma^*) \quad \dots \dots \quad (4)$$

where  $H_o = H(\sigma^*)$  is the total activation energy and  $v^* = -\frac{dH}{d\sigma} (\sigma^*)$  is the activation volume. Substituting equation (4) in equation (2), we have,

$$\dot{\epsilon} = \dot{\epsilon}_o \exp\left(-\frac{H_o}{v^*} - \frac{kT}{v^*} I_n \left(\frac{\epsilon}{\dot{\epsilon}_o}\right)\right). \quad \dots \dots \quad (5)$$

In many cases ' $\dot{\epsilon}_o$ ' and ' $H_o$ ' can be assumed constant and  $\sigma^*$  and  $v^*$  are functions of strain only. A direct indication of equation (5) is that, plastic flow stress should decrease linearly with increase in temperature and increase logarithmically with increase in strain rate.

2.3. A similar constitutive equation, reported by Akulov<sup>3</sup> for plastic flow, is

$$\dot{\epsilon} = C_1 U^* (\sigma - \sigma_k) + C_2 U \cdot \frac{d\sigma}{dt} + \frac{1}{E} \cdot \frac{d\sigma}{dt} \quad \dots \quad (6)$$

which in effect governs the process of formation, movement multiplication and destruction of dislocations. Here  $U^*$  is the concentration of mobile unit dislocations which can move when  $\sigma$  is constant,  $C_1 = \frac{b_o}{w}$ ,  $b'$  is the Burgers vector, and  $\frac{\sigma - \sigma_k}{w}$  is a quantity proportional to the rate of movement of mobile dislocations. If plastic flow takes place under shear stresses the modulus of elasticity is replaced by ' $G$ ' the shear modulus.

2.4. Gilmans<sup>4</sup> proposes a model for the analysis of dynamic equilibrium of a dislocation line, which is mathematically expressed by  $F_d = F_i + F_v$   $\dots \quad (7)$

where the driving force  $F_d = \sigma_s b$  is caused by the applied stress which tends to move it forward, and the inertial force  $F_i = m \cdot a$  opposes it along with the viscous drag force  $F_v = B \cdot V$ . Here ' $\sigma_s$ ' is the applied stress, ' $b$ ' the elementary (Burgers) displacement, ' $m$ ' the effective mass, ' $a$ ' is the acceleration, ' $V$ ' the velocity of motion, and  $B$  is the damping constant assuming linear (Newtonian) viscosity. So

$$\begin{aligned} \sigma_s b &= m \cdot a + B \cdot V \\ &= m \cdot \frac{dv}{dt} + B \cdot V. \end{aligned} \quad \dots \quad (8)$$

solving for ' $V$ '

$$V(t) = \frac{\sigma_s b}{B} \left[ 1 - \exp \left( -\frac{B}{m} \cdot t \right) \right] \quad \dots \quad (9)$$

Initially when the stress is applied ( $t=0$ ) the velocity of the dislocations is zero. Subsequently it increases to a rate determined by the acceleration coefficient ( $B/m$ ).

As the velocity increases, the viscous drag force approaches the magnitude of the driving force. Consequently the acceleration gradually becomes smaller and finally a steady state value is reached where the steady state velocity is given by

$$V_{ss} = \sigma_s b / B \quad \dots \quad (10)$$

For a pure metal, taking the approximate values  $B \approx 10^{-3}$  poise ;  $b = 3 \text{ \AA}$  ;  $m = \rho b^2$  where  $\rho = 8 \text{ grams/m}^3$ , the steady state value of velocity for an applied stress of 100 ata is  $V_{ss} = 3 \times 10^3 \text{ cms/sec.}$ , which should be reached within a time of  $7 \times 10^{-12} \text{ sec.}$  Because of such a short and rapid transient it can be proposed that during this short interval the dislocations are in steady-state motion. In addition the arrestive period of the dislocation at the barriers is shortened. But dislocations multiply when in motion and hence there can be relatively long periods of transient plastic flow in a specimen taken as a whole.

**2.5.** Regenerative processes in crystal structure during plastic deformation increases dislocation density. This increase tends to facilitate further flow. Simultaneously this increase in plastic flow tends to be inhibited by intersection of mobile dislocations with other dislocations or lattice defects, the frequency of interaction increasing with the population density. This requires an increase in the applied stress to sustain the motion. The increase in applied stress causes dislocations to circumvent the obstructions by cross slip, climb or appearance of jogs. After large straining of materials, whole blocks of the material become re-oriented and glide planes no longer remain flat. This causes immobilisation of dislocations giving rise to strain hardening.

**2.6.** Kumar *et al*<sup>5</sup> define four distinct regions, (Fig. 1), in the deformation process for a metal subjected to increasing strain rate and tem-

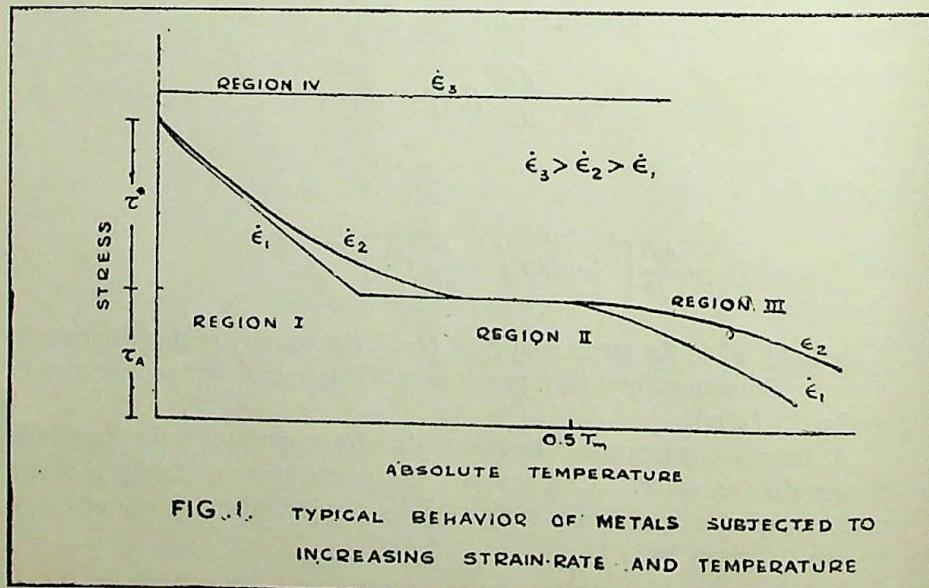


FIG. 1. TYPICAL BEHAVIOR OF METALS SUBJECTED TO INCREASING STRAIN-RATE AND TEMPERATURE

perature. Each of these regions is associated with a class of dislocation mechanism shown in Table 2.

TABLE 2.—CLASSES OF DISLOCATION MECHANISMS (after Kumar *et. al*<sup>5</sup>)

Class	Characteristics	Examples
1. Thermally activated (Activation energy less than $50kT$ ), including diffusion controlled mechanisms.	Flow stress that decreases with an increase in Temperature or decrease in strain rate. $\gamma \propto \exp\left(-\frac{u}{kT}\right)$	1. Peierls process. 2. Intersection. 3. Rapid solid solution hardening. 4. Cross slip. 5. Motion of jogged screws. 6. Climb of edges. 7. Viscous creep due to solute atom interaction.
2. Athermally activated (Activation energy greater than $50 kT$ ).	Flow stress that are insensitive to temperature and independent of strain-rate. $\frac{\dot{\tau}}{G} \propto f(\gamma)$	1. Long range stresses. 2. High local stresses. 3. Short range order alloys. 4. Suzuki locked alloys.
3. High Velocity Damping mechanisms (Viscous damping).	G=Shear modulus. Strain rate is proportional to over stress, $(\dot{\tau} - \dot{\tau}_B)$ . $\gamma \propto (\dot{\tau} - \dot{\tau}_B)$	1. Thermo-elastic. 2. Phonon scattering. 3. Phonon viscosity. 4. Electron viscosity. 5. Dislocation-dislocation damping. 6. Dislocation-impurity damping.

The plastic strain rate is equivalent to

$$\epsilon p = \rho \cdot b \cdot V = N \cdot A \cdot b \cdot v \quad \dots \quad (11)$$

where ‘ $\rho$ ’ is the mobile dislocation density, ‘ $b$ ’ the Burgers vector, ‘ $V$ ’ the mean velocity, ‘ $N$ ’ the number of points where dislocations are arrested by barriers, ‘ $A$ ’ the area swept out per activation and ‘ $v$ ’ the frequency of thermal activation.

In FCC metals the Peierls stresses are low. The flow stress can be written as

$$\tau = \tau_A + \tau^* + \frac{BV}{b} \quad \dots \quad (12)$$

where ' $\dot{\tau}_A$ ' is the athermal component, ' $\tau^*$ ' the thermally activated component,  $\frac{BV}{b}$  is the contribution from the viscous damping mechanism and 'B' the viscous drag coefficient.

The number of activation points 'N' and the area of activation 'A' are assumed independent of stress and the frequency of activation is given by

$$\nu = v^\circ \cdot \frac{b}{L} \cdot \exp\left(-\frac{U}{kT}\right) \dots \quad (13)$$

where  $U = U_j - \tau^* \cdot L b^2$ ,  $\tau^* = \tau - \tau_A$ , 'L' is the spacing of dislocations, 'U' is the energy required by thermal activation to complete intersection and 'U<sub>j</sub>' is the energy required to form a jog. Hence it can be seen that the activation energy is the jog energy minus the work done by the local stress during intersection.

Combining the equations we have ;

$$\dot{\tau} = \dot{\tau}_A + (U_j/Lb^2) + (kT/Lb^2) \ln(\epsilon p \cdot L/b^2 N A v^\circ) \dots \quad T \leq T_c \dots \quad (14)$$

and  $\tau = \tau_A \dots \quad T \geq T_c \dots \quad (15)$

which suggests a linear relation between  $\dot{\tau}$  and  $\ln(\epsilon p)$ .

If the applied stress is higher than the flow stress at 0°K in the thermally activated region, then the intersection can be completed instantaneously and continuously without the aid of thermal fluctuations. The dislocation velocity in these cases is limited by the various energy dissipative damping mechanisms.

In BCC metals extensive work has been done on Iron and Steel and a limited amount of work on molybdenum and tantalum. Molybdenum has the particular advantage that it does not exhibit phase transition as the other BCC metals. In addition the activation volume (of about  $10b^3$ ) for BCC iron, molybdenum and tantalum is smaller than for FCC metals and hence the flow stress for the former is more strain-rate sensitive.

Though BCC and FCC metals are easily formed either cold or hot, the deformation of HCP metals with poorest ductility and the least number of slip planes is of the greatest interest for explosive forming technology. Titanium and Zirconium with prism slip planes and Magnesium, Cadmium and Zinc with basal slip planes come under this category. A number of investigators have predicted a high temperature dependence and a significant strain rate sensitivity of flow stress. It is also significant that rate of work-hardening increases with temperature contrary to what is predicted by recovery mechanism.

**2.7.** Explosive Hot Forming experiments with tool steels and refractory metals conducted by Haegland<sup>6</sup> and others indicate the advantages of such a process from the metallurgical point of view, under restricted conditions of plastic flow. An additional advantage inherently obtained is the hardening of the workpiece.

Experiments of Van Wely and Verbraak<sup>7</sup> with reference to shock loading of metals also provides sufficient support to these predictions. A large amount of work has been done on behaviour of single crystals under loading conditions similar to those encountered in Explosive forming.

### 3. 0. CONCLUSIONS

Summing up, the necessity of detailed investigations into the kinetics and mechanisms of dislocations is more important, especially in the region of strain rates and loading conditions encountered in HERF processes, since there does not seem to be a more convincing way of explaining the behaviour of metals formed explosively. Till recently the results of tests conducted on uni-axial tensile specimens under impact loading were being held good enough for analysing the explosive and other HERF processes. This is neither true nor justified since the resulting stresses are distinctly different. Similar is the authors' view with regard to the results obtained from experiments conducted on single crystals. The HERF processes could immensely benefit only when detailed studies are undertaken with a view to controlling the rates of loading, temperatures and other process parameters to give the optimum advantages in formability criteria.

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## THE ENLIGHTENED PUBLIC AND CORONARY HEART DISEASE

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RARELY a day passes without hearing the death news of some important person due to coronary heart disease. In fact it is now the commonest cause of death for people beyond the age of 40 years. In India coronary heart disease accounts for about 20 per cent of all cases of heart disease. More alarming is the fact that with the rise in longevity of our population due to efficient control of infectious diseases, cardiovascular disease, in general, coronary heart disease in particular, has become more definitely the dominant cause of death. The over-all mortality from acute coronary heart diseases is as much as 60 per cent. Out of this 10 per cent die before receiving any medical aid ; 25 per cent die within first 48 hours ; another 20 per cent within next fortnight and the rest 5 per cent in the next four weeks. Not only this but also there is a great increase in the morbidity in the survivors and the subsequent longevity is limited to few years. It might seem possible that the high incidence of coronary heart disease at the present time may be due to improved diagnostic techniques and the increased consciousness of the disease. But apart from these the incidence of the disease is obviously rising as can be seen from the fact that there has been a 15 per cent rise in the number of deaths due to coronary heart disease between the years 1940-1955 and Martin (1956) has shown that during the past 10-15 years the age standardised death rate from this disease has become double and at some ages has even been trebled. Though actual consolidated figures from India are not available there can be no doubt that the incidence of "Coronary death" is rapidly rising.

### NATURE OF CORONARY HEART DISEASE

The syndrome of coronary heart disease is produced by a process of gradual narrowing and thickening of the coronary arteries so that circulatory disturbances of the myocardium are produced. When the circulatory disturbance is transient the person suffers from angina pectoris and there is no permanent damage to the heart muscles. On the other hand when the circulatory insufficiency is more prolonged, a picture of acute coronary insufficiency results with more prolonged and more severe attack of cardiac

pain but still there is no necrosis of myocardium. When the circulation is so severely impeded that heart muscle is necrosed then a picture of myocardial infarction emerges.

#### MECHANISM OF INSUFFICIENCY

For the last several decades every conceivable discipline of medicine has been pressed into service in a determined effort to ascertain the causes and course of coronary artery disease only with limited success. Just what brings about the narrowing of the coronary arteries is uncertain but possibly the essence is a process of atherosclerosis, in which mixture of cholesterol crystals and other lipid substances called plaques of atheroma get deposited on the inner layer of the arteries causing narrowing and inside ulceration of arteries. The other possibility is that the narrowing of the coronary arteries is brought about by deposition of platelet plugs inside the vessels due to some cause or other. These being the current concepts it is quite reasonable to briefly discuss these two concepts.

#### CONCEPT OF LIPID IMBIBITION

Lipid materials like cholesterol, fatty acids, phospholipids and lipoproteins are normally circulating in the blood. It has been suggested that these lipids are normally being imbibed through the arterial wall and are being removed by the lymphatics from the wall. If there is increased amount of lipid transfer into the vessel wall or diminished removal by the lymphatics then the obvious result will be a deposition of the lipid in the intimal tissue. These lipid deposits form the atheromatous plaques and narrow the vessels and may become fibrosed later on. Lipid deposition is favoured by three factors, namely, increased level of lipid in the plasma, raised intravascular pressure favouring passage of lipid through the arterial wall and a structural or functional abnormality of the vessel wall. All these factors will be discussed at length later.

Another theory proposes that the macrophages of the reticulo-endothelial system engulf lipid material forming foam cells and for some reason migrate to the vessels wall. There they get deposited, disintegrate and form the atheromatous plaques. On the other hand imbalance in the colloidal dispersion of plasma has been implicated for the lipid deposition.

#### THROMBOGENIC CONCEPT

Abnormal platelet behaviour has recently drawn wide attention as the cause of intravascular thrombosis. Platelets bear an opposite charge to that of the intimal surface of the vessel wall and are, therefore, normally kept suspended in the blood. If some factor alters this electric charge of either the platelet or the intimal surface of the vessels then platelet deposition

occurs. Under such circumstances platelet microthrombi form on the intimal surface of the vessel and some are incorporated to form atheroma like lesion. An increased lipid content of plasma has been shown to provoke such changes.

These being the fundamental processes leading to narrowing of the coronary arteries, it is convenient to consider some of the predisposing and precipitating factors which contribute to it.

#### 1. Age :

Though in western countries the highest incidence of coronary heart disease is in the seventh decade, in India it makes its appearance earlier in life and the peak incidence is attained between 51 and 60 years. This is possibly related to the higher longevity of the western people. Coronary heart disease was previously being thought to be an usual consequence of the generalised degenerative process of aging. But now-a-days precocious heart disease before the age 40 years has widely been reported especially from various parts of India. Sen *et al* (1970) have noted coronary heart disease even at ages of 13 and 14 years. It is reasonable at present to think that the mechanism of coronary heart disease in such younger group is different. Possibly congenital abnormalities of the coronary arteries are contributory factor.

#### 2. Sex :

The general sex ratio obtained from various studies is 4 : 1 in favour of males. In India the general sex ratio has varied from 3.5 : 1 (Vakil, 1962) to 24 : 1 (Singh *et al*, 1965). However there is a striking change in the sex ratio in the various age groups. Thus in the age group of 30 to 44 years the M : F ratio is 13 : 1, whereas between the ages of 45 and 62 years the ratio is only 2 : 1 and beyond the age of 70 years the proportion is equal. This discrepancy obviously suggests the protective role of female sex hormones. In fact there is great rise in the incidence of coronary heart disease in premenopausal age group in whom menopause has been artificially induced. On the other hand male predominance has been explained by other means. Thus it has been related to the smoking habit in males or to more frequent exposure of males to competitive stresses of industrialised urban life. A difference in the internal construction of the vessels in the two sexes might also be a contributing factor.

In recent years the fear of increase in the incidence of coronary heart disease in females has been expressed due to wide use of oral contraceptives. It has been suggested that the "pills" increase platelet adhesiveness and promote thrombosis of the coronary arteries. However these effects are more on the veins and the real hazard if any, awaits more elaborate studies.

*3. Socio-economic Status :*

Banerjee (1958) reported that 77.4 per cent of the intellectual class of the society consisting of lawyers, businessmen, engineers, doctors and professors suffered from coronary heart disease. Reports from Madras (Vytilingam, 1964) also showed 68.7 per cent incidence in higher social group. Contrary to these reports it is interesting to note that Krishnawsamy *et al* (1970) in a survey of railway workers noted 31.3 per cent incidence of the disease. Similar reports have appeared from other parts of the country which suggest that coronary heart disease is no more confined to the higher socioeconomic group. If any predilection really exists it is possibly related to the dietary difference and the sedentary habits.

*4. Physical Activity :*

Though scanty reports like that of Krishnaswamy *et al* have shown higher incidence of coronary heart disease amongst manual workers, it is widely held that physical exercise protects from coronary heart disease. Thus Chattopadhyaya *et al* (1969) noted that amongst the cases of ischaemic heart disease 77.7 per cent were from the persons with sedentary habits. On the other hand it is also true that coronary atherosclerosis may be precipitated in vigorous athletes in later life if they fail to maintain a high level of physical activity.

*5. Regional difference :*

In India the lowest incidence (6 per cent) is seen in Himachal Pradesh in contrast to 23 per cent of Uttar Pradesh. Similarly Japanese who have migrated to U. S. A. have a much higher mortality than those resident in Japan. High incidence has also been reported in the Yemenite emigrants to Israel and Indian emigrants abroad. A racial difference has also been noted as is evident from the high incidence in western European races as compared to the native Bantus of Africa. It seems that such differences are mainly due to difference in the diet constitution, the western diet consisting of much more fat.

*6. Heredity :*

The difference in the pattern of coronary heart disease has often been explained by postulating that the disease is hereditary and transmitted genetically. In a retrospective study (Gertler *et al*, 1954) it was seen that 37.1 per cent of the fathers of patients with coronary heart disease had died of the same as compared to 18.5 per cent in the control. However apart from statistical data there is little at hand to support this view.

*7. Smoking :*

Cigarette smoking has often been incriminated for the premature onset of coronary heart disease and this has also been offered as an important

factor for the higher incidence in the males. In one study of India (Banerjee, 1958) moderate to heavy smoking could be associated in 64.4 per cent of cases of coronary heart disease. The death rate due to this disease in America is in excess by 60,000 per year amongst the smokers beyond the age of 40 years. Tobacco smoking has transient vasoconstrictive action on the coronary arteries which may prevent adequate coronary circulation. Also continued smoking has been shown to favour a rise in the blood fatty acid level. Both these factors might be complementary in the production of coronary atherosclerosis.

#### 8. *Coffee :*

Mild to moderate coffee consumption may have a dilatory action on the coronary vessel but there is statistical association between intemperate coffee consumption and high incidence of coronary heart disease.

#### 9. *Emotional State :*

Coronary heart disease has been found to be more frequent in those with great ambition, compulsory striving, extreme competitiveness, a drive for recognition, preoccupation with deadlines and a deep sense of guilt and anxiety about work and leisure. The higher incidence of coronary disease in the industrialised and more advanced areas have been ascribed to such stresses. This is probably mediated through alteration in the lipid metabolism.

#### 10. *Obesity :*

Traditionally obesity and high incidence of coronary heart disease have been accepted as close associates. The obese have a 40 per cent greater chance of developing the disease as compared to the normal.

#### 11. *Hypertension :*

High blood pressure has been noted in 50-52 per cent of coronary heart disease in India (Naik *et al*, 1966 ; Chattopadhyaya *et al*, 1969). A six fold increase in the incidence of coronary heart disease occurs among those having a blood pressure over 180 mm. Hg. as compared to persons having blood pressure under 120 mm. Hg. systolic. High blood pressure presumably predisposes to atherosclerosis by mechanical trauma to the vascular intima which serves as nidus for lipid deposition. It also serves as the driving force for transferring blood lipids into the arterial wall.

#### 12. *Personality pattern :*

Considering all above factors a composite picture has been drawn to engross all the predisposing conditions in one man. Such a hypothetical person may conveniently be termed as a "Coronary man". He is typically a middle aged or older male with a thick set physique, obesity and short

stature. He is usually a heavy smoker with sedentary habit often with hypertension or diabetes and a particular environment of emotion anxiety and other stresses.

The true nature of coronary atherosclerosis is considered to be a disturbed internal metabolism embracing mainly that of lipid and carbohydrate and being influenced by such factors as diet and hormones.

### 13. *Abnormal lipid metabolism :*

An elevation of all lipid fractions of blood have been noted in patients with overt coronary heart disease. The main fractions which have been considered significant are cholesterol, neutral fatty acid, triglycerides and lipo-proteins. In a study from Madras it was shown that in 50 per cent of cases of coronary heart disease the serum cholesterol level was more than 250 mg. per cent. Similarly the Framingham study (1962) indicated that the risk of coronary heart disease in young man was approximately six times higher in those whose cholesterol was more than 260 mg. per cent than in those whose levels were less than 220 mg. per cent. Reports have been consistent with these views throughout the world. The fact emerges that the incidence of coronary heart disease is particularly low when the serum cholesterol is below 200 mg. per 100 ml.

Elevated serum triglyceride levels have also been correlated with high incidence of coronary atherosclerosis in South African Europeans as compared to the native Bantus. Low density lipo-proteins of particular floatation values have also been found to be raised in persons with clinical coronary heart disease.

There has been recent interest in the possible role of free fatty acid in the production of coronary atherosclerosis. Detailed analysis of the fatty acid composition of the cholesterol esters, phospholipids, triglycerides and lipo-proteins show that in all the lipid fractions the proportion of saturated fatty acids (without any double bonds in the molecule) is greater and that of polyunsaturated ones (with many double bonds in the molecules) smaller in patients with coronary disease than in normal control. This ratio has been found to be important and attempts have been made to increase the proportion of polyunsaturated fatty acids by feeding in order to reduce the incidence of coronary heart disease.

The role of raised serum cholesterol in the causation of coronary heart disease becomes more clear when one considers the high incidence of the disease in cases of familial hypercholesterolaemia. Since the chief source of blood liquids is diet, it needs close attention.

### 14. *Diet :*

High incidence of coronary heart disease runs parallel with high fat and cholesterol intake. It is accepted that the actual amount of fat rather than cholesterol in the diet influences serum lipid and cholesterol levels. The

higher incidence of coronary heart disease in western countries, European races and in the high socio-economic group is related to the high fat content of their diets.

There is increasing evidence that the actual composition of fat in diet has a considerable bearing. A high animal fat content (which consists mainly of saturated fatty acids) in the diet is more harmful. When animal fat in the diet is substituted by fat from vegetable sources (which consists mainly of polyunsaturated fatty acids) the serum cholesterol is eventually lowered. Statistical evidences point to the fact that vegetarians have a significantly lower serum lipid level and lower incidence of coronary heart disease as compared to non-vegetarians.

#### *15. Role of abnormal Carbohydrate metabolism :*

Diabetes is complicated with coronary heart disease with unusual frequency. Conversely overt diabetes is seen in 21-23 per cent of cases of coronary heart disease (Chattopadhyaya, 1969 and Sen *et al*, 1970). Family history of diabetes in patients with coronary heart disease is also quite high. Even when overt diabetes is not present abnormal glucose tolerance can be demonstrated in a high proportion of cases of coronary heart disease. It is now widely held that the vascular abnormality in diabetes is inherited similar to and independent of the abnormal glucose tolerance. Excess of sugar consumption has also been implicated in the aetiogenesis of coronary atherosclerosis. It is believed that platelet adhesiveness is increased by the raised glucose level in the blood and this favours atherosclerosis as has been discussed earlier. The diabetic state is also associated with high serum free fatty acid and triglyceride level which as we have seen has direct bearing on the incidence of coronary atherosclerosis.

#### *16. Hormonal influences :*

The higher incidence of coronary atherosclerosis in males and oophorectomised (with ovaries removed) females have been ascribed to lower circulating oestrogen levels in the blood. Hypothyroid and hypopituitary states are known to be associated with high serum cholesterol level and coronary atherosclerosis. Similarly Cushing's syndrome and cortisone administration has been associated with high serum cholesterol levels which may predispose to coronary atherosclerosis. A hormonal influence also seems to be partly responsible for high incidence of the disease in diabetes. All the hormonal influences are probably mediated through an alteration in the lipid metabolism.

#### *17. Management of coronary heart disease :*

Recent developments in this field like artificial cardiac pace maker and cardiac transplantation have great promise but are only successful in a few.

Therefore it is only the preventive measures which have the greatest scope in the ultimate management of coronary heart disease.

Preventive measures known at present are control of serum lipid levels by diet and drugs ; control of diabetes, hypertension and obesity ; and avoidance as far as possible such precipitating factors like smoking, sedentary habits and excessive stress. Amongst these the main stay of treatment is the dietetic control of obesity and serum lipid levels.

#### D I E T

Ample evidences point to the fact that if obesity and serum cholesterol levels are controlled by dietary fat restriction, improvement in the status of coronary heart disease patients is striking. However such a diet may be able to reduce the incidence of coronary atherosclerosis but does not influence the mortality rate. Inspite of this, strict implementation of dietary regimen is highly desirable.

A satisfactory regimen is a diet consisting of 35 to 40 per cent of fat and of slightly lower calorific value. Of the fat atleast twice the amount should be from vegetable sources as compared to that of animal sources. Small frequent feedings are more beneficial. The vegetable fats that are available readily at present are corn oil, ground nut oil, soya bean oil, and sunflower oil. The diet should also be restricted in such pure carbohydrates like sucrose and glucose. Fruits and vegetables can be taken. Fish, both lean and fat and lean meat as chicken can be taken. Egg yolk contains much cholesterol and the diet should not contain more than 2 to 4 eggs per week preferably without the yolk.

Weight reduction is recommended for all over weight patients but especially for those who are either suffering from coronary heart disease or are prone to it.

Such diet restriction should be started quite early in life by the beginning of second decade for a successful prophylaxis. Every person beyond 35 years of age who are coronary prone should be extended unsolicited dietary advice. In New York "Anti-coronary" clubs have been developed which extend such advice.

However, strict diet restriction alone is not always successful and is sometimes difficult to follow. Under such circumstances drugs which can reduce serum cholesterol level are of help especially when the serum cholesterol reduction is less than 15 per cent of the basal level inspite of strict dietetic regimen. It is worth while discussing few of the important drugs.

#### D R U G S

1. *Nicotinic acid* : This is a vitamin of the B-complex group and exerts a serum cholesterol lowering action when administered in daily doses

of 3 to 6 Gms. The side effects are minimal when it is started in doses of 1 Gm. daily and then gradually increased.

2. *Clofibrate* : It is available as Atromid. In doses of 2 Gm. per day it has serum lipid lowering action and is quite safe and effective when used along with diet restriction.

3. *Dextrothyroxine* : It is well known that patients with hyperthyroidism usually have low serum cholesterol level whereas patients with hypothyroidism have markedly elevated levels. Obviously then, Dextrothyroxine (Choloxin) has been used in doses of 2 to 8 mg. daily for the reduction of serum cholesterol level when it is elevated. However its use in coronary heart disease cases may precipitated anginal attacks and extreme care is needed in such cases.

4. *Cholestyramine* : This is an anion exchange resin that binds bile acids in the gut and thus prevents fat absorption. It is relatively non-toxic and has been used in doses of 8 to 32 Gms. per day in divided doses.

5. *Oestrogen* : The relative immunity of premenopausal women from coronary heart disease has led to extensive trial of oestrogenic substances in the prevention of coronary artery disease. However they are potentially faminizing in males and hence their wide use has not been accepted.

Other agents like plat sterols (sitosterol), triparanol, and heparin have also lipid lowering action but are seldom used either due to large doses required or to very short duration of action.

Apart from attempts to lower serum lipid levels smoking should be drastically stopped and diabetes and hypertension rigidly controlled.

The efficacy of any of these measures in the prevention and treatment of coronary atherosclerosis is as yet un-proved. Many of these recommended measures deserve and are undergoing further investigation.

#### CONCLUSION

In conclusion the enlightened public should examine the vital issue, be well advised to have physical and biochemical annual check-ups after 40 years of age, should cut down calories to maintain standard or preferably rather substandard weight, reduce animal fat from the daily diet and practise moderate amount of physical exercise.

Tobacco in any form promote vascular disease and should be avoided. Alcohol in moderation may be permissible for occasional use. Latent diabetes of maturity onset type should be specially looked for and if detected be kept under control by modern treatment by which it is meant that unscientific treatment may stop glycosuria but may keep-up a raised blood sugar level thus giving a false sense of security.

In no other disease the maxim "Prevention is better than cure" is more appropriate that coronary heart disease yet it is so difficult, long drawn out and well calculated skilled a process.

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## SYNTHESIS OF SOME ANTHRONE DERIVATIVES

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**I**N the present investigation several amino-methyl derivatives have been synthesised from anthrone and 6-chlore anthrone.

Several beta amino ketones and amino-methyl derivatives have been reported to possess antispasmodic activity (Ann. Rav. Biochem. 1943, 13,549, J. Amer. Chem. Soc. 1949, 2048, J. Inst. of Chem. 109, 1968). It has also been reported that the presence of sulphur-containing groups may promote the antispasmodic activity (J. Amer. Chem. Soc. 1944, 66, 1645 and Nature. 1950, 166, 122). In view of the biological and pharmacological importance of thiazoles, pyridines and pyrimidines it was considered worthwhile to prepare some amino-methyl derivatives from anthrones and study their antispasmodic and antihistaminic activities.

The anthrones were prepared from their corresponding anthraquinones by reduction with tin and Conc. HC1. in acetic acid medium.<sup>1</sup>

Amino-methyl derivatives were prepared by condensing the anthrones with various 2-amino heterocyclic compounds and para-formaldehyde in benzene and hydrochloric acid according to Sen and Madan *et. al.*<sup>2</sup> and the Mannich bases were collected.

Further studies on pharmacological tests of these compounds and studies on structure activity correlation are in progress.

### EXPERIMENTAL

#### *General procedure for the preparation of amino-methyl derivatives :*

A mixture of anthrone (0.01 M.) and para-formaldehyde (0.01 M.) in dry benzene (25 ml.) was taken in a conical flask and refluxed for about 30 minutes.

It was then acidified with 5-10 drops of Conc. HC1 and the mixture was refluxed for further 8-10 hours, during which the Mannich base hydrochlorides separated as fine crystalline mass in most of the cases. After completion of the reaction the mixture was cooled and the crystalline mass

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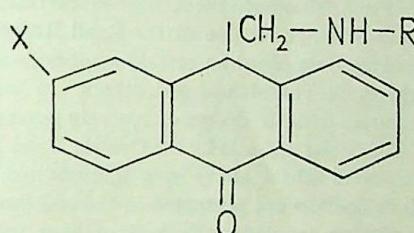
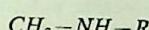
<sup>1</sup> A. I. Vogel, Page 740.

<sup>2</sup> J. Ind. Chem. Soc., 355, 5, 1957.

was filtered at the pump ; washed with dry benzene and then with ether and then basified by  $\text{NH}_4\text{OH}$  and finally crystallised from ethanol.

The analytical data and m. p. etc., of Mannich bases derived from anthrones and 6-chloroanthrone prepared by following the above procedure are given in the table below.

TABLE.—AMINOMETHYL DERIVATIVES DERIVED FROM ANTHRONES



Nature of X	Nature of R.	Yield %	M. P. °C	Mol. Formula	% of Nitrogen	
					Found	Calculated
H	2-pyridyl.	49	210	$\text{C}_{21}\text{H}_{16}\text{N}_2\text{O}$	8.73	8.97
H	2-pyrimidyl.	50	205	$\text{C}_{20}\text{H}_{15}\text{N}_3\text{O}$	13.28	13.41
H	2-Xanthyl.	55	>250	$\text{C}_{28}\text{H}_{19}\text{O}_3\text{N}$	3.12	3.35
H	2-benzothiazolyl	55	180	$\text{C}_{22}\text{H}_{16}\text{ON}_2\text{S}$	7.35	7.36
H	2-(4-phenyl) thiazolyl.	60	245	$\text{C}_{24}\text{H}_{18}\text{ON}_2\text{S}$	6.98	7.33
Cl	2-pyridyl.	50	195	$\text{C}_{21}\text{H}_{15}\text{N}_2\text{OCl}$	7.89	8.11
Cl	2-xanthyl.	54	7250	$\text{C}_{28}\text{H}_{18}\text{O}_3\text{NCI}$	2.86	3.09
Cl	2-benzothiazolyl.	59	192	$\text{C}_{22}\text{H}_{16}\text{ON}_2\text{SCl}$	6.92	7.17
Cl	2-(4-phenyl) thiazolyl.	55	234	$\text{C}_{24}\text{H}_{17}\text{ON}_2\text{SCl}$	6.39	6.72
Cl	2-(4,5-diphenyl) thiazolyl.	60	145	$\text{C}_{30}\text{H}_{21}\text{ON}_2\text{SCl}$	5.21	5.69

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# A REVIEW OF TEMPERATURE STUDIES ON CONCRETE PAVEMENTS

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(Received on 23 August 1971)

Temperature studies on concrete pavements have been made in some Western countries over a period of last 50 years, while studies in India are taken up recently. Some of the experimental investigations were made by the U. S. Bureau of Public Roads, at the Arlington test track and other state highway departments of U. S. A. and at the Road Research Laboratory, London. Theoretical analysis based on certain assumptions were attempted by H. M. Westergard, S. Timoshenko and others. In India, research for collection of temperature data for design of concrete pavements, was undertaken at the I.I.T. Kharagpur and also by the Central Road Institute, Delhi. A brief review is made of all the above investigations and the comparative nature of the various findings are presented at the end through graphs and tables. Recommendations are made on the basis of these analysis, for further work in this field.

## INTRODUCTION

CEMENT concrete pavements are constantly exposed to the direct effect of climatic conditions like temperature, humidity and moisture. An exposed slab gets alternately heated and cooled. The transmission of temperatures to the slab occurs through direct incidence of Sun-Rays, by radiation from the surrounding air and from the subgrade on which it lies. Depending on the construction details like slab area and thickness and the material used in the slab, a distribution or dispersion of the temperatures takes place through its area and thickness. The rise and fall in the uniform temperatures and the formation of temperatures gradients across the depth are the important factors to be included in the rational design of pavement thickness and the joints and the choice of suitable type and construction of subgrade for supporting the slab. All these factors make a strong plea for temperature studies. Many theoretical and experimental studies on temperature variations and effects in concrete pavements have been made by researches abroad and in India, of which a comprehensive review is made in this article.

## STUDIES ABROAD

The earliest studies on the behaviour of concrete pavements was probably made by the U. S. Office of Public Roads in 1910, which conducted some laboratory and field experiments to study the effects of expansion and con-

traction of concrete pavements. Based on studies made, A.T. Goldbeck (1919 U. S., B. P. R.)<sup>1</sup> and Clifford Older (1921 Illinois P. W. D.) independently derived equations for thickness of concrete pavements for corner loads, accounting for the loss of support at corners as a result of weak, subgrades and temperature and moisture differentials. These concepts become the basis for many formulas in current use. Older found that the extent of transverse warping varied according to the width of slab and it was reduced by more than 50% in two-Lane pavement pannel slabs using a longitudinal joint, centrally.

H. M. Westergaard was the first to make theoretical analysis of stresses and deflections in concrete road slabs produced by wheel loads and also by variations of temperatures<sup>2</sup>. He investigated for stresses at the three critical regions (corner, edge and interior) in the slabs under two main considerations viz., (1) Slow seasonal changes of temperatures assuming to be uniform throughout the thickness and (2) quick changes of temperature gradient from top to bottom and constant temperature at neutral plane of slab. Equations were given by him for stresses and deflections in case of broad and long slabs, and long and narrow slabs in rectangular pannels, assuming linear temperature gradient.

Bradbury developed equations for temperature warping stresses along edges and interior of slab on the basis of Westergaard's analysis and E. F. Kelly made elaborate stress measurements in concrete pavements, to correlate the actual values with the results from Westergaard's formula. The latter recommended modified and compact formula for maximum tensile stresses in concrete pavements due to corner, edge and interior loading.

Since 1930 the U. S., B. P. R. carried out extensive investigations at the Arlington Experimental Farm (Virginia) and in addition to others, the research was planned to include study of the effect of temperature and moisture conditions on the size, shape and load carrying ability of pavement slabs. The investigations were carried out on a group of 10 full size ( $40' \times 12'$ ) pavements with different cross sections and joint design, but keeping uniformity of concrete and the subgrade. The details of findings were reported by Teller and Sutherland<sup>3</sup> in a series of articles in "Public Road" (1935). Concluding on the temperature studies they stated that for the pavement sizes used certain stresses arising from restrained temperature warping are equal in importance to those produced by maximum wheel load. In some cases the stresses amounted to 350 psi and 125 psi. in the longitudinal and transverse directions.

F. N. Sparkes of Road Research Laboratory, London showed that stresses produced in concrete slabs by (a) loading (b) restrained temperature warping and (c) friction could be computed from theoretical considerations.<sup>4</sup> Also he reported some experimental work carried out at the R. R. L. during 1937-40 meant to verify the theoretical values based on Westergaard's theory. Two slabs of 4 feet squares and 6" and 9" thickness were used for tem-

perature studies, which showed that temperature gradient is not necessarily a straight line as assumed by Westergaard. Sparkes states that in certain conditions the stresses due to restrained temperature warping may be approximately of double the magnitude of stress caused by subgrade restraint to horizontal movement.

J. Thomlinson of R. R. L., London, developed a theory<sup>5</sup> on the basis of non-linear temperature gradient. The theory is based on the conception that temperature at a point in the slab is dependent on the factors, instantaneous surface temperature, depth, time and previous temperature history of the slab and that the concrete slab is a semi-infinite solid. If the heat supplied to a semi-infinite solid is such that the surface temperature variation is sinusoidal and given by

$$\theta = \theta_0 \sin \frac{2\pi t}{T} \quad \dots \quad (1)$$

then the temperature at any instant on a plane at any depth is given by

$$\theta = \theta'_0 e^{-\frac{x}{h}\sqrt{\pi/T}} \sin \left( \frac{2\pi t}{T} - \frac{x}{h} \sqrt{\pi/T} \right) \quad \dots \quad (2)$$

the equation (1) being only a particular case of equation (2) where  $\theta$  denotes the temperature on a plane at a distance 'X' from the surface at time 't',  $\theta_0$  denotes the amplitude of daily or annual cycle of variation of the exposed surface temperature, T is the periodical time of temperature cycle (24 hours for daily cycle and one year for seasonal analysis) and  $h^2$ =diffusivity of concrete (0.009 c. g. s., units as given by Thomlinson).

Thomlinson illustrated through graphs the variation of temperature with time at various depths and variation with depth at various times. Based on these the temperature distribution equations were developed for finding internal temperature stress, stresses due to end restraint and warping restraint. His experimental verification also indicated the correctness of simple harmonic variation of temperature at surface on hot summer days and not so on dull days and during nights. Stewart Champion suggests<sup>6</sup> the analysis of non-simple harmonic variation curves into harmonics and then to calculate the individually created component stresses and phase them to get the true value of temperature stress.

J. H. Swanberg conducted experiments<sup>7</sup> on 16½' × 17' experimental slab 7" thick at University of Minnesota and studied temperature variations in the pavement as well as the subgrade over a period of 5 years (1940-45). Both seasonal and daily changes were observed by incorporating 6 numbers of thermocouples in slab and 5 numbers into the subgrade. All the salient figures about the surface and air temperature, average slab temperature and those of subgrade were given in his report.

An eleven year study (1934-45) was made by R. A. Moyer<sup>8</sup> at Iowa State College in which measurements were taken for opening and closing of Joints. Nine types of expansion joints using materials such as premolded asphalt, cork, sponge, rubber, poured asphalt and steel were tried and the values measured. Blow up failures at peak summer periods were also observed, which indicated compression failure under buckling. These were attributed to high temperatures in slabs and growth (volume change due to chemical or physical changes) in concrete as main reasons. Bradbury pointed out that maximum contractions due to daily cycle of temperature variation and not the seasonal value should be used in evaluation of subgrade restraint. Geldmacher experimentally showed that some times deflection due to warping exceeded those induced by superimposed loads.

S. Timoshenko<sup>9</sup> developed an equation for stress due to restrained temperature conditions, at a depth 'X' in a concrete slab, by applying theory of elasticity and assuming the slab to be homogeneous, isotropic elastic and semi-infinite. The general form of the equation for the stress is

$$\sigma_t = \frac{eE\theta'_x}{1-\mu} + \frac{1-ke}{d(1-\mu)} \int_0^d eE\theta'_x \, dx \\ + \frac{12(\frac{d}{2}-x)(1-kw)}{d^3(1-\mu)} \int_0^d eE\theta'_x \left( \frac{d}{2} - x \right) \, dx$$

Where  $\theta'_x$  = temperature of slab at depth 'X' over a uniform value.

$d$  = Thickness of slab in inches.

$Ke$  = Coefficient of end restraint.

$Kw$  = Coefficient of warping restraint.

$\mu$  = Poissons ratio for concrete.

#### TEMPERATURE STUDIES IN INDIA

Studies were mainly conducted by the Central Road Research Institute—at some Master stations in India and at the Indian Institute of Technology, Kharagpur, the results of which will particularly prove very useful for humid tropical countries where no temperature data seems to be available for concrete roads.

At the I. I. T. Kharagpur investigations were carried out during the period 1959-64 on experimental cement concrete slabs. Effects of temperature variations on a 4" thick and 33'×12' size concrete pavement, bounded to a water bound macadam base were studied<sup>10</sup> and reported at the proceedings of the R. I. L. E. M. held in July, 1960 at a Hafia (Israel). Also effects of temperature variations were studied on 6" slab 5'×4' size laid on 4" thick w. b. m., base over 6" laterite soling. Slab temperatures and air temperatures were measured in the hottest part of the year, on the normal

as well as black painted slab. The macadam base was found to act as an integral part of C. C. slab as far as temperature variation was concerned. The maximum positive and negative temperature gradients and their timings were recorded.

A comparative study was undertaken by the author (of this review) on 4", 6" and 8" thick experimental slabs laid on natural subgrade, at the same institute in 1963.<sup>11</sup> The temperatures were measured over a period of 3 months on representative days, by means of copper-constant on thermocouples. From the observed results, relations were established between values of amplitudes of surface temperature with their corresponding amplitudes of air shade temperature variations and also between the respective maximum and minimum values.

The maximum positive temperature gradient occurring at about 1 p. m. was found always nearly linear. The values of maximum positive and negative values could be assumed as 2°C and 1°C respectively per inch depth of slab. It was estimated that a uniform rise up to 25°C in 4" slab and upto 20°C in case of 6" and 8" slab can take place. A study was also made on a 15'×12' slab, 6" thick, for comparing the theoretical and observed daily expansions and contractions and the effect of the subgrade on it. Other aspects recorded in the above studies were the type of variations and the gradients, time of occurrence of neutral gradient and the effect of subgrade on the slab temperature etc. The combined results on the various aspects of studies made at the I. I. T. Kharagpur including those by the author are separately reported.<sup>13</sup>

Temperature studies were conducted at 7 Master stations, (Trivandrum, Calcutta, Madras, Hyderabad, Jullunder, Delhi and Poona in India by the C. R. R. I., Delhi during 1962-65.<sup>12</sup> Based on the studies on 10'×10' size of 4", 6", 8", 10" and 12" at all other stations and one each of 12'×10' size of 2", 3", 4", 6", 8", 10" and 16" laid at Delhi, suggestions for the values of temperature differentials to be adopted at different parts of India are given.

It was reported that maximum temperature differentials in India are by and large higher than the figures reported from Western countries and also certain conclusions were drawn on the values and timings of maximum positive and negative temperature gradients to be assumed for design.

#### C O M P A R I S O N O F S O M E O F T H E S T U D I E S

Only a broad and general outline of the studies made abroad and in India have been given. The following tables (1) and (2) the figures (1) and (2) indicate the comparative nature of the specific results of these studies.

The various results tabulated indicate that more or less the features of temperature variations as observed by studies at the I. I. T., Kharagpur and those made by the C. R. R. I., at seven master stations go close to each other.

TABLE I.—FEATURES OF TEMPERATURE OBSERVATIONS

Place of Study.	Period of study.	Slab thickness included in study.	Shape of Temperature variation.	Shape of Temp. gradient.	Occurrence of Air shade temp.	Occurrence of slab surface temperature.	Time of occurrence of Maximum +ve. temp. gradient.	Time of occurrence of Maximum -ve. temp. gradient.	Time of neutral temp. gradient.
			Peak.	Others.	Max.	Min.	Max.	Min.	
I. I. T., Kharagpur.	1960-63	4", 6" and 8" inches.	Nearly Sinusoidal during day but irregular in night time.	Linear. Non-Linear.	2 P.M. to 6 A.M.	4 A.M. to 6 A.M.	5 A.M. to 6 A.M.	1 P.M. to 10 P.M.	Around Midnight.
C.R.R.I. (India) at seven Master Stations.	1962-65	5, 7.5, 10, 15, 20, 25, 30, and 40 cms.	Not Sinusoidal after the peak temperature.	Nearly linear.	Curved. 1 P.M. to 3 P.M.	Early Morning. to 2 P.M.	1 P.M. to 2 P.M.	—	Around Noon.
U. S. A.	1920-45	6 and 7 inches.	—	—	—	—	—	—	4 A. M. to 5 A. M.
Road Research Lab. (London) U. K.	1935-39	6 and 9 inches.	Sinusoidal (Thomlinson)	Curved.	—	—	—	—	—
Sweden (Bergstrom).	Before 1950	6 inches.	Surface temperature depicted as a function of slab thickness.	—	—	—	—	—	8-30 A.M.

TABLE 2.—CRITICAL VALUES OF TEMPERATURE OBSERVATIONS AND RELATIONS

Place.	Maximum slab Temperature observed.	*Ratio of (Amplitude of Surface Temp.)		(Max. $\frac{\theta_a \text{ max.}}{\theta_a \text{ min.}}$ slab Temp.).	Ratio of† (Min. slab Temp.).	Maximum +ve temp. gradient.	Maximum -ve temp. gradient.	Maximum rise or fall in Uni- form slab temperature.
		Amplitude of Air shade Temp.)	Amplitude of variation.					
I. I. T., Kharagpur.	54.8°C (131°F) May 1963 29% More for black painted slab.	5.52°C (daily) 10.3°C (seasonal)	1.98 to 2.28.	1.43.	1.5.	0.90 to 1.14.	1.00. 2.10°C per inch. depth.	1.66°C to 2.0°C per inch. depth.
C. R. R. I., (India) at seven Master Stations.	57°C (135°F) New Delhi. Poona.	10.15°C (seasonal)	—	1.74 (Tri- vandram) whole period.	—	—	3.8°C per inch. for 4" slab at Poona.	2.6°C to 4.5°C for various regions and thick- nesses.
U. S. A.	112.5°F (44.5°C) Arlington 122°F (50°C) Swanson.	—	—	—	—	—	1°F to 3°F per inch. (Kelly). (Swanson).	1°F to 3°F per inch. (Swanson). 1°F to 3°F per inch. (Swanson). 1°F to 3°F per inch. (Swanson).
U. K.	104°F (40°C) June 1942.	—	3.5 to 4.0 (Stewart champion).	—	—	—	—	—
Sweden.	88°F (31°C) Bergstrom.	—	—	—	—	—	—	—

\*  $(\theta_a \text{ max} - \theta_a \text{ min}) / (\theta_a \text{ max} - \theta_a \text{ min.})$ .  
†  $\theta_a \text{ min.} - \theta_a \text{ min.}$ .

Obs.—Observed value.  
Rec.—Recommended value.

FIG. 1 TEMPERATURE VARIATIONS IN 6 INCHES THICK SLAB

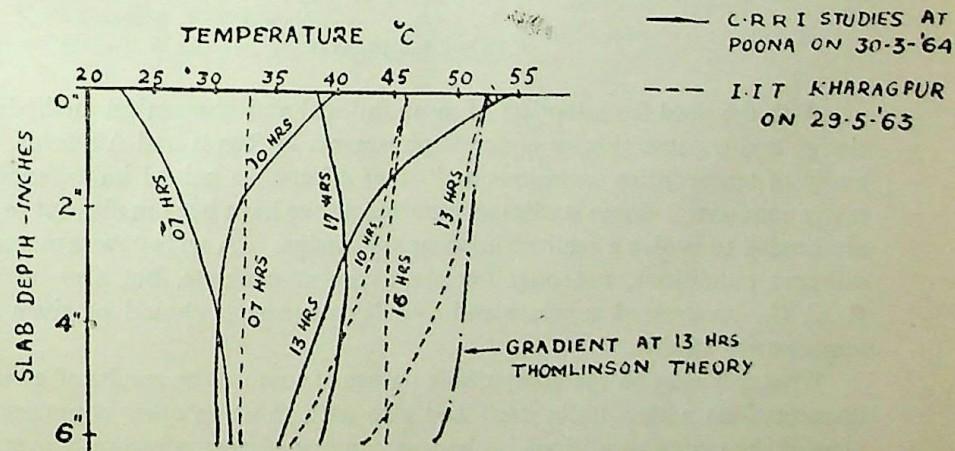
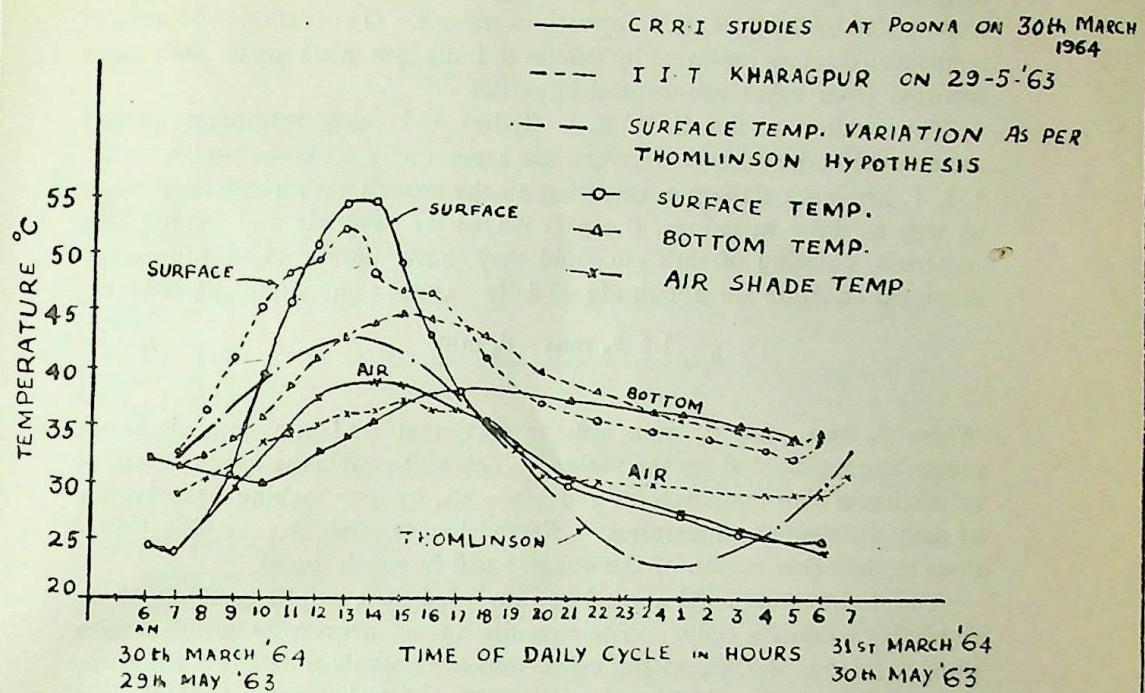


FIG. 2 TEMPERATURE GRADIENTS IN 6" SLAB

Obs.—Observed value.  
Rec.—Recommended value.

\*  $(\theta_a \max - \theta_a \min) / (\theta_a \max - \theta_a \min)$ .  
†  $\theta_a \min - \theta_a \min$ .

The results of the later are more specific as they cover the different regions of the country. The surface temperatures, time of critical occurrences do almost coincide, but the value of maximum recommended positive temperature gradient of  $2^{\circ}\text{C}$  for Kharagpur is far less than the values recommended by the C. R. R. I. for various regions. On the whole the critical temperature values indicated by studies in India, are much higher than those reported from other sub-tropical countries.

The studies at the C. R. R. I. (India) and other researches abroad as reported in the references cover a few aspects only while the studies at the I. I. T. are more elaborate, involving all the aspects such as seasonal effect as well as daily variations, the part played by subgrade and base course materials, painting of slab etc., and they have pioneered to suggest an empirical equation for amplitude of daily surface temperature variation as

$$\theta_o = \frac{1.5 \theta_a \text{ max} - \theta_a \text{ min.}}{2}$$

Where  $\theta_a \text{ max.}$  and  $\theta_a \text{ min.}$  are the maximum and minimum air shade temperatures recorded for the region. This will enable the ready depiction of maximum slab temperatures and gradients, by only making observations of daily air shade temperatures. Establishment of similar empirical relations in the other region of the country will be much useful.

The studies conducted abroad and reviewed here, will be useful for those respective countries only. Their results do not necessarily correlate with those from our studies, as the conditions are entirely different. However, they had been very useful in projecting the type of studies necessary and their importance. The studies initiated in India on the lines set by the I. I. T., Kharagpur and the C. R. R. I. create a basis for further investigations.

#### CONCLUSION

With the need for adoption of more rational and economical methods of design and construction of concrete pavements in Roads and Air fields, the study of temperature variations and other effects has gained importance in many countries. Some studies as reported above have been made, but more are needed to evolve a realistic approach of design. A wide coverage under different conditions, not only for plain cement concrete, but also on the R. C. C., prestressed concrete and over-lay pavements should be given for temperature studies.

Whatever may be the comparable nature of some of the results of general investigations within India itself and also with those in other countries, in view of the varied conditions in the vast country of ours, a region-wise study as per geographical location, the subgrade nature and the construction methods and other typical conditions influencing the design, would be very much essential. Scope exists for the studies to be conducted in the

arid zones (Rajasthan) and also Himalayan region of the country, on the effect of such climates on concrete pavements.

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## STUDIES ON CHALKONE DERIVATIVES AS FUNGICIDES

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IN our present investigation a number of chalkone derivatives have been prepared from different substituted acetophenones and their fungicidal activities have been evaluated.

In our earlier communication<sup>1</sup> the infra-red spectra of a number of chalkones and their acetyl and methoxy derivatives have been reported for the study of structure-spectra correlations. The present investigation describes the preparation of dibromo compounds and flavones of different substituted chalkones with a view to studying their fungicidal activities using *pericularia oryzae* as the test fungus, which causes the most destructive disease in the wheat plant.

The chalkones used for the preparation of different derivatives were prepared by following the procedure of Rout *et. al.*<sup>1</sup>

The dibromo compounds of some of the above chalkones, were prepared by the addition of bromine to the solution of chalkone in acetic acid.

The flavones were prepared from the dibromides by using 10 N sodium hydroxide as the condensing agent.

The tests for fungicidal activity was performed using *pericularia oryzae* as the test fungus. Some of the typical compounds of each of the above series (described in the experimental section) have been tested for their fungicidal activity.

### EXPERIMENTAL

#### *General procedure for the preparation of chalkone dibromides :*

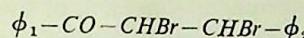
Chalkone (0.01 M) was dissolved in acetic acid (8 ml.) and 25% bromine in acetic acid solution (2 ml. W/V) was added and kept overnight. The coloured solid separated was crystallised from acetic acid. The analytical data, m. p. etc., of different chalkone dibromides are given in the Table I.

#### *General procedure for the preparation of flavones :*

Chalkone dibromide (0.01 M) was dissolved in alcohol (10 ml.) and 10 N. sodium hydroxide solution (3 ml.) was added. The mixture was kept over-

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1. J. Ind. Chem. Soc., 507, 41, 1964.

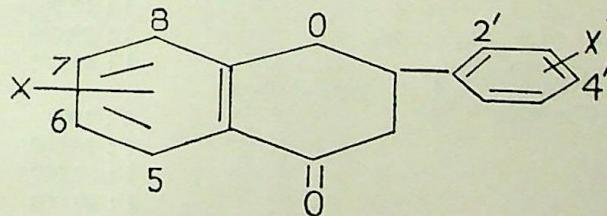
TABLE I



Sl. No.	Nature of $\phi_1$	Nature of $\phi_2$	Yield %	M.P. °C	% of bromine		
					Found	Calcd.	
1	3-Chloro	2-hydroxy phenyl	Phenyl	30	144	38.12	38.23
2	-do-		p-Tolyl	45	138	36.86	36.99
3	-do-		o-Chloro phenyl	35	140	35.16	35.32
4	-do-		2,4-Dichloro phenyl	30	167	—	—
5	-do-		o-Hydroxy phenyl	35	100	36.28	36.79
6	5-Chloro	2-hydroxy phenyl	Phenyl	30	156	38.20	38.23
7	-do-		p-Tolyl	30	151	36.76	36.99
8	-do-		o-Chloro phenyl	40	149	35.12	35.32
9	-do-		2,4-Dichloro phenyl	45	147	—	—

night and in some cases for 72 hours and then it was acidified with 50% hydrochloric acid. The solid separated was crystallised from alcohol. The analytical data m. p. etc., of the different flavones prepared by the above procedure have been recorded in the Table-II.

TABLE II



Nature of X	Yield %	M. P. °C	% of chlorine	
			Found	Calcd.
8-Chloro	50	128	13.32	14.64
8,2'-Dichloro	20	137	24.19	24.37
8-Chloro 4'-methoxy	60	121	12.39	12.48
8-Chloro 2'-hydroxy	50	170	13.02	12.80
6-Chloro	60	93	13.11	13.64
6,2'-Dichloro	30	94	24.21	24.37
6-Chloro 4'-methoxy	20	87	11.96	12.18

*Fungicidal tests :*

Some of the typical compounds from each of the above series (Tables—I and II) have been screened for assaying their fungicidal properties by the method of Montogomery and Moore<sup>2</sup>. The fungus used was *pericularia oryzae* and the time of incubation allowed was six hours.

The test results reveal the following order of activity :—Chalkone dibromide>Chalkone>Flavone.

Results of the fungicidal tests of some of the derivatives of Chalkones :

TABLE III

Sl. No.	Name of the compounds.	Dilution.	% of spore germination in test slide.
1	2'-Hydroxy 3'-chloro C*	1 : 1000	80
2	2'-Hydroxy 3'-chloro chalkone dibromide	1 : 1000	0
		1 : 10,000	0
		1 : 20,000	16
		1 : 40,000	48
3	2'-Hydroxy 3'-chloro 4-methoxy chalkone dibromide	1 : 1000	0
		1 : 10,000	8
		1 : 20,000	12
		1 : 40,000	30
4	2'-Hydroxy 3', 2-dichloro chalkone dibromide	1 : 1000	0
		1 : 10,000	0
		1 : 20,000	6
		1 : 40,000	20
5	2'-Hydroxy 3', 2, 4-trichloro chalkone dibromide	1 : 1000	0
		1 : 10,000	0
		1 : 20,000	0
		1 : 40,000	10
6	2'-Hydroxy 5'-chloro C	1 : 1000	75
7	2'-Hydroxy 5'-chalkone dibromide	1 : 1000	0
		1 : 10,000	6
		1 : 20,000	12
		1 : 40,000	36
8	2'-Hydroxy 5', 2-dichloro chalkone dibromide	1 : 1000	0
		1 : 10,000	0
		1 : 20,000	2
		1 : 40,000	8
9	8-Chloro flavone	1 : 1000	100
10	8,2'-Dichloro flavone	1 : 1000	96

C—denotes chalkone.

2. MONTOGOMERY AND MOORE.—(J. Pomol. Hort. Sci., 15, 235, 1933).

Thus 2'-hydroxy 3'-chloro chalkone dibromide (compound No. 2) inhibits 84% spore germination in a concentration of 1 : 20,000 where as 2'-hydroxy 3'-2 dichloro chalkone dibromide (compound No. 4) and 3',2,4-trichloro 2'-hydroxy chalkone dibromide (compound No. 5) which possesses extra chlorine atoms than the former inhibits spore germination to an extent of 80% and 90% respectively at a dilution of 1 : 40,000, which indicates that the increase in halogen contents reinforce the fungicidal activity.

The authors are grateful to Dr. S. Y. Padmanavan, Mycologist, Central Rice Research Institute, Cuttack for his help in carrying out the fungicidal tests in his laboratory.

# THERMOANALYTICAL STUDIES OF URANIUM (IV) FORMATES

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Thermal decomposition of uranium (IV) formates,  $\text{UO}(\text{HCOO})_2 \cdot 1.5 \text{ H}_2\text{O}$  and  $\text{U}(\text{HCOO})_4$  have been studied employing DTA and TGA techniques in air and  $\text{CO}_2$  atmosphere. The most striking observation made during the study is the formation of  $\text{UO}_2$  as the penultimate product when the oxyformate is heated in  $\text{CO}_2$  atmosphere at  $\sim 360^\circ\text{C}$ .

## INTRODUCTION

THE preparation of uranium (IV) oxyformate,  $\text{UO}(\text{HCOO})_2 \cdot 1.5 \text{ H}_2\text{O}$  and tetraformate,  $\text{U}(\text{HCOO})_4$  was reported by us earlier.<sup>1,2</sup> It has been also reported that  $\text{UO}_2$  can be obtained to an extent of 90% by the thermal decomposition of uranium (IV) oxyformate in vacuo at  $\sim 500^\circ\text{C}$ . So far, no thermoanalytical studies of these compounds have been carried out in greater detail. The present communication deals with the thermal decomposition of uranium (IV) formates, employing DTA and TGA techniques.

## EXPERIMENTAL

The compounds were prepared according to the methods reported earlier.<sup>1,2</sup> The thermoanalytical studies by TGA and DTA techniques of the compounds were carried out in the equipments assembled by the authors. For thermogravimetric analysis, sample sizes weighing about 0.1 gm. were used and pyrolysis in static air and continuously flowing  $\text{CO}_2$  atmosphere and at a furnace heating rate  $5^\circ\text{C}-6^\circ\text{C}$  per minute. For differential thermal analysis, the heating rate of the furnace was  $10^\circ\text{C} \pm 1^\circ\text{C}$  per minute.

## RESULTS AND DISCUSSION

### Uranium (IV) oxyformate, $\text{UO}(\text{HCOO})_2 \cdot 1.5 \text{ H}_2\text{O}$ .

The TGA and DTA curves for uranium (IV) oxyformate in air and  $\text{CO}_2$  atmosphere are shown in Fig. 1 (a, b) and 2 (a, b). The profile of

the thermograms indicate a very complex course of decomposition. The TGA studies in air show that the decomposition in the oxyformate begins at  $\sim 80^\circ\text{C}$  and is complete at  $\sim 310^\circ\text{C}$ . The weight loss in the region  $80-185^\circ\text{C}$  takes place at a relatively slow rate and the weight loss at  $185^\circ\text{C}$  where a break occurs in the curve approximates to the loss of 1.5 mole of water per mole of the compound. The dehydrated product in turn undergoes decomposition at a comparatively higher rate and yields  $\text{U}_3\text{O}_8$  at  $\sim 310^\circ\text{C}$ . In this region of the thermogram two breaks in the curve have been observed at  $\sim 210^\circ\text{C}$  and  $\sim 285^\circ\text{C}$  respectively. However, they are not well defined and it has not been possible to assign any reasonable stoichiometric formula to these metastable intermediates. That the final product was  $\text{U}_3\text{O}_8$  has been further confirmed by pyrolysis of the residue in a platinum crucible outside the furnace in air.

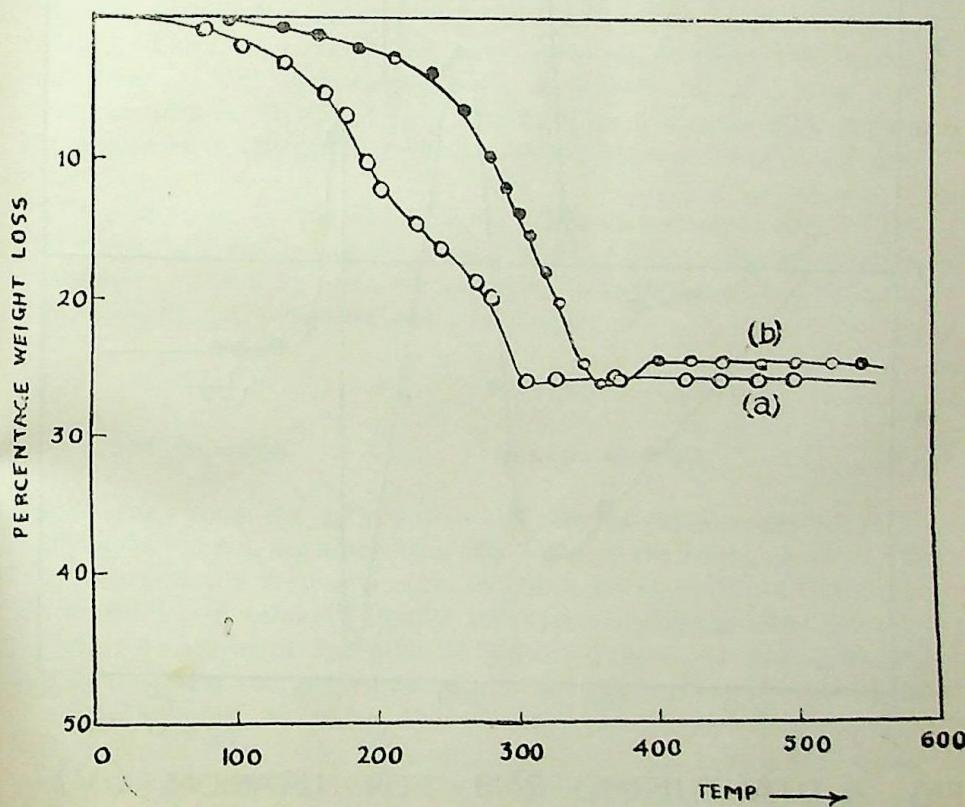


FIG 1 TGA THERMOGRAM FOR URANIUM (IV)  
OXYFORMATE (a) IN AIR (b) IN CARBONDIOXIDE

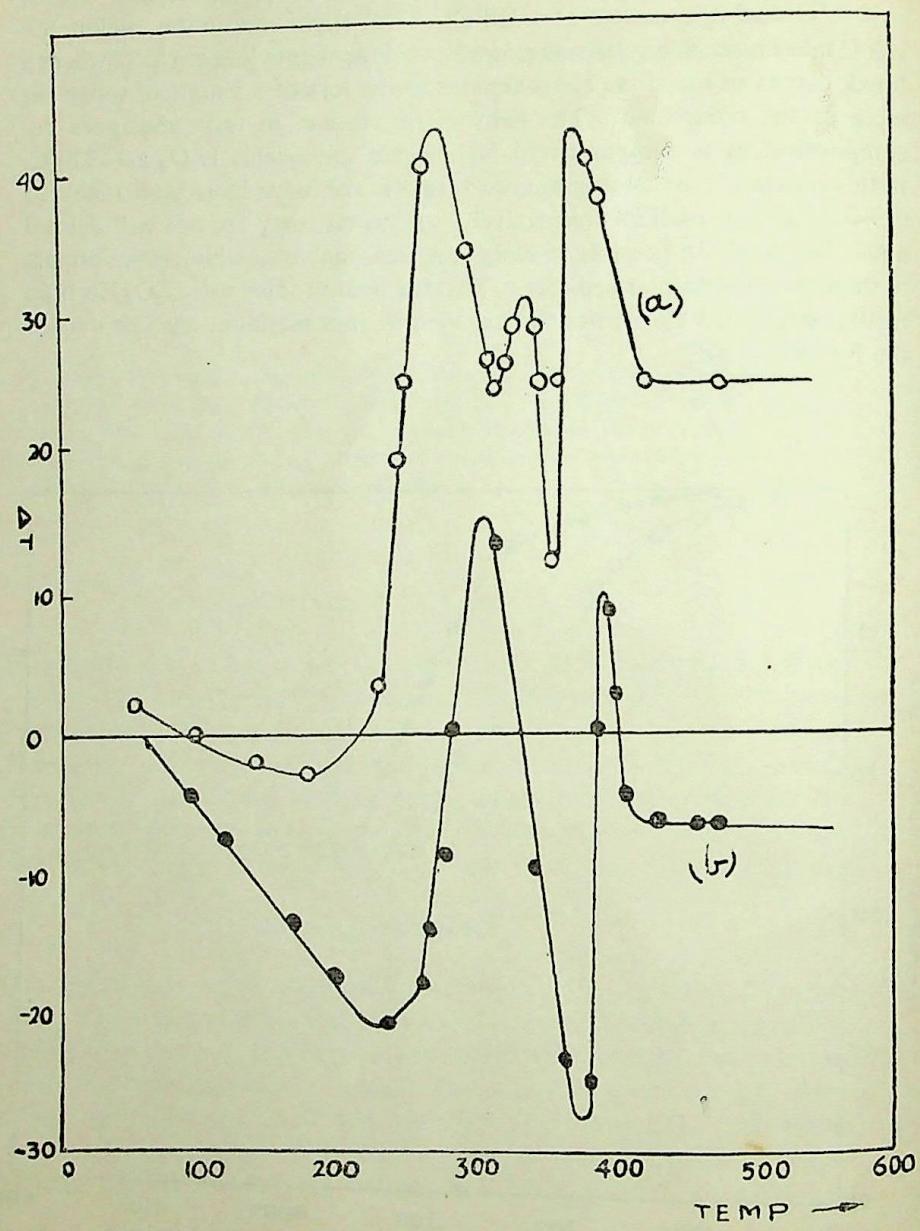
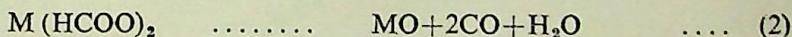


FIG 2 DTA THERMOGRAM FOR URANIUM (IV)  
OXYFORMATE (a) IN AIR (b) IN CARBONDIOXIDE

When the decomposition of the oxyformate is carried out in  $\text{CO}_2$  atmosphere, the reaction begins at a higher temperature and follows a different course of reaction. It seems that deaquation and decomposition occur right from the commencement of the reaction  $\sim 90^\circ\text{C}$  and  $\text{U}_3\text{O}_8$  is obtained as the final product at  $400^\circ\text{C}$ . The reaction is sluggish upto  $240^\circ\text{C}$  after which it undergoes decomposition in a single step and gives  $\text{UO}_2$  at  $\sim 360^\circ\text{C}$ . The uranium dioxide as is obtained in the thermogram, subsequently gains in weight and is oxidised to  $\text{U}_3\text{O}_8$  (due to the presence of small quantities of air in  $\text{CO}_2$ ).

The DTA thermogram in air of the oxyformate has three endothermic peaks, with peak temperatures at  $180^\circ\text{C}$ ,  $320^\circ\text{C}$  and  $360^\circ\text{C}$  respectively and two exothermic peaks at  $225^\circ\text{C}$  and  $380^\circ\text{C}$  respectively. The first endothermic peak is due to deaquation of the compound. The overall decomposition process in the intermediate stage as is seen in DTA involve the combination of two reactions i. e., oxidation of  $\text{UO}_2$  to  $\text{U}_3\text{O}_8$ . The DTA involves the combination of two reactions i. e., oxidation and decomposition and final exothermal peak at  $\sim 380^\circ\text{C}$  is attributed to oxidation of  $\text{UO}_2$  to  $\text{U}_3\text{O}_8$ . The DTA curve in  $\text{CO}_2$  atmosphere, shows slight shift in peak temperatures. Two endothermic peaks at  $210^\circ\text{C}$  and  $380^\circ\text{C}$  and two exothermic peaks at  $310^\circ\text{C}$  and  $410^\circ\text{C}$  have been observed in the DTA curves. The sequences of the peaks are almost in the same order as in the case of air.

The difference in behaviour of the thermal decomposition of the oxyformate in air and in  $\text{CO}_2$  atmosphere seems to involve different reaction mechanism. Metal formates are known to decompose in two different ways, such as (for a divalent metal formate).



Besides  $\text{CO}$ ,  $\text{CO}_2$ ,  $\text{H}_2$ , and  $\text{H}_2\text{O}$  other decomposition products, such as formaldehyde etc., are also found, depending on the nature of the metal ion.<sup>3,4</sup> In case of uranium formates, an additional reaction i. e., oxidation of uranium (IV) to uranium (VI) state takes place during the decomposition process. Therefore, the formation of  $\text{UO}_2$  or  $\text{U}_3\text{O}_8$  would depend on the rate of oxidation and decomposition. If the decomposition takes place at a faster rate than oxidation,  $\text{UO}_2$  would be predominantly formed than  $\text{U}_3\text{O}_8$  and vice versa. The TGA thermogram in  $\text{CO}_2$  atmosphere shows a depression at about  $360^\circ\text{C}$  due to the formation of  $\text{UO}_2$  and its subsequent oxidation to  $\text{U}_3\text{O}_8$ . In view of this observation, the reaction in  $\text{CO}_2$  atmosphere is regarded to involve a higher rate of decomposition than oxidation and hence formation of  $\text{UO}_2$  is favoured, which is obtained as the penultimate product.

*Uranium (IV) Tetraformate, U(HCOO)<sub>4</sub>:*

The TGA and DTA thermograms of uranium tetraformate in air and CO<sub>2</sub> atmosphere are shown in Fig. 3 (a, b) and 4 (a, b) respectively. The results obtained from the thermo-analytical studies indicate that the decomposition process involves complex chemical reaction. The TGA study in air shows that the weight loss of the compound begins at  $\sim 95^{\circ}\text{C}$  and is complete at  $\sim 380^{\circ}\text{C}$  finally forming U<sub>3</sub>O<sub>8</sub>. Initially the compound decomposes at a slower rate in the temperature range 95-200°C and the rate becomes comparatively faster in the range 200-340°C. A near horizontal peak is seen from 340-360°C and the weight loss in this region corresponds to the formation of an intermediate UO<sub>2</sub>CO<sub>2</sub>. This composition is assumed on the basis that UO<sub>2</sub> is known to be highly basic and therefore might interact with the acidic gas CO<sub>2</sub> in the region 360-380°C. The compound decomposes very fast to U<sub>3</sub>O<sub>8</sub>.

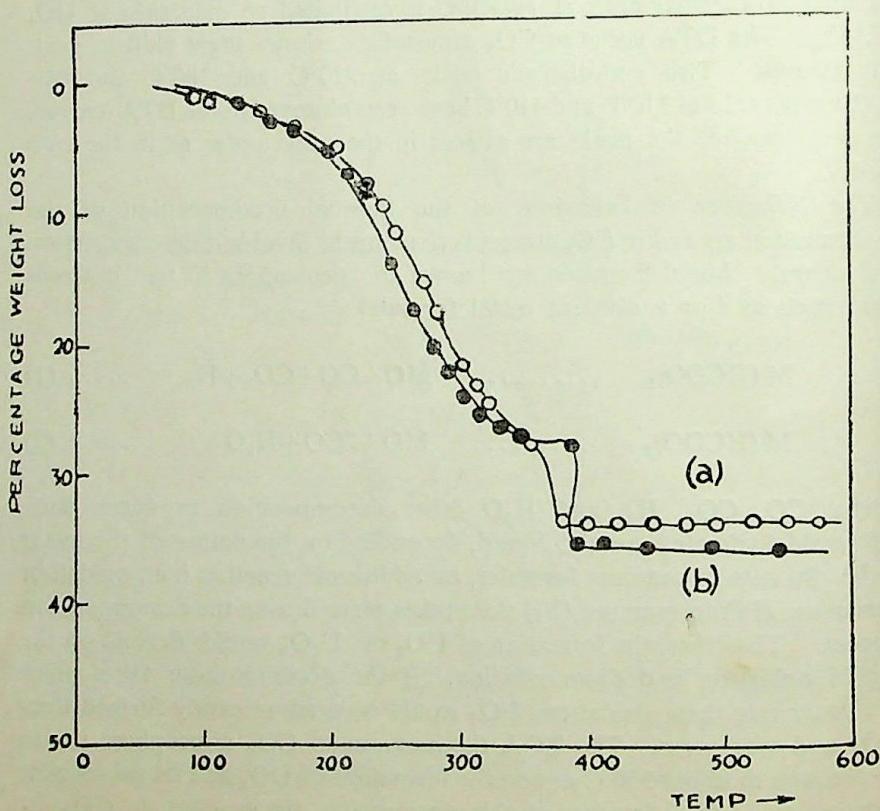


FIG 3 TGA THERMOGRAM FOR URANIUM (IV) TETRAFORMATE (a) IN AIR (b) IN CARBONDIOXIDE

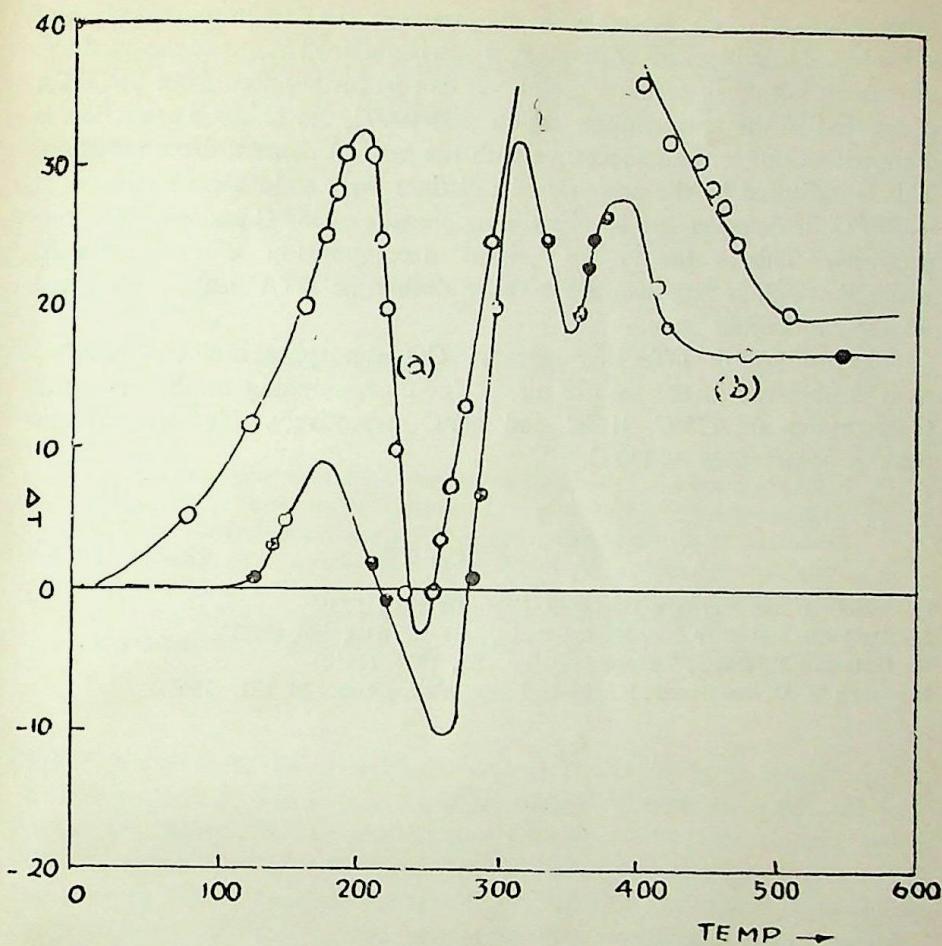


FIG 4 DTA THERMOGRAM FOR URANIUM (IV)  
TETRAFORMATE (a) IN AIR (b) IN CARBONDIOXIDE

The decomposition in CO<sub>2</sub> atmosphere seems to follow the same course of reaction. As is observed in the present case, there occurs a drag of the curve towards higher temperature and the horizontal plateau corresponding to the UO<sub>2</sub>CO<sub>2</sub> covers a wide range from 340 to 390°C.

The DTA curve in air shows three exothermic peaks at peak temperatures 200°C, 330°C and 390°C and two endothermic peaks at 240°C and 365°C situated near about the same transition temperatures as is observed in TGA. The initial exothermic reaction cannot be simply explained by simple dissociation reaction, since such reactions are endothermic in nature. The exothermicity of the reaction most probably arises due to superimposition of

other reactions such as oxidation of uranium (IV) to uranium (VI) and solvation of uranium ions with water, which is obtained as one of the products of decomposition of formate group. It can be further seen from the DTA curve that in the temperature region 300-400°C, the oxidation reaction is competitive rather than successive with the normal thermal decomposition. This is indicated by the presence of a distinct weak endothermic minima at  $\sim 370^\circ\text{C}$  in between the two exothermic peaks  $\sim 350^\circ\text{C}$  and  $\sim 380^\circ\text{C}$  respectively. This is due to the thermal decomposition of undecomposed material which is responsible for the endothermic DTA peak, superposed on the exothermic peak.

The profile of the DTA thermogram in  $\text{CO}_2$  atmosphere is almost the same as it is observed in the case of air. The corresponding exothermic peak temperatures are  $175^\circ\text{C}$ ,  $315^\circ\text{C}$ , and  $385^\circ\text{C}$  respectively. The endothermic peak is observed at  $\sim 260^\circ\text{C}$ .

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STUDIES ON BOROHYDRIDE REDUCTION—PART-I.  
KINETICS OF SODIUM BOROHYDRIDE REDUCTION  
OF  $\alpha$ ,  $\beta$ -UNSATURATED KETONES

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(Received on 29 September 1971)

The kinetics of sodium borohydride reduction of  $\alpha$ ,  $\beta$  unsaturated ketone (chalcone) has been studied in isopropyl alcohol. The reaction is found to be first order with respect to the ketone and first order with respect to sodium borohydride. The parameters of the transition state theory has been determined. The result has been compared with the borohydride reduction of saturated ketones. A new mechanism in the light of the isolated product has been suggested for the borohydride reduction of  $\alpha$ ,  $\beta$ -unsaturated ketones.

THE rate of accretion of organic molecule reactivity data having direct thermodynamic and kinetic significance has increased strongly over the past several years. In the present past a number of reactions have been utilised in studies of the effects of structure on the reactivity of aldehydes and ketones. These include the reaction of these compounds with hydroxy amine, phenyl hydrazine, and semicarbazide. However, the available evidence indicates that the mechanism of these reactions involves a number of stages and it is not always clear that the same step is the rate determining. The difficulty has handicapped the exploration of the influence of structure on carbonyl group reactivity in some cases. The mechanism is rather confusing. The observations that the borohydride reaction appears to be simple, kinetically suggested that it might provide a means of circumventing these difficulties. A search of the relevant literature indicates that although the kinetics of sodium borohydride reduction of a number of simple ketones and steroid ketones have been studied, no attempt has yet been made for the kinetics of borohydride reduction of  $\alpha$ ,  $\beta$  unsaturated ketone. Since the reagent is particularly interesting in its use for the synthetic investigation of a number of steroids and  $\alpha$ ,  $\beta$ -unsaturated keto steroids, we wish to report the kinetics of the borohydride reduction of chalcones (in  $\alpha$ ,  $\beta$ -unsaturated ketone) which may provide valuable evidences regarding the mechanism.

The reaction of sodium borohydride with chalkone exhibits simple second order kinetics, first order in borohydride and first order in carbonyl derivatives. Thus the reaction rate can be represented

$$\text{Rate} = k_1 [\text{ketone}] [\text{NaBH}_4].$$

#### EXPERIMENTAL

Solutions of chalkone 0.005 (M) and sodium borohydride 0.05 (M) in isopropyl alcohol were stored in a thermostatic bath. The borohydride solution (25 ml.) was then added and the time was commenced in half addition. After thorough mixing, 10 ml. of the sample was withdrawn at suitable interval of time and added to a mixture of 1 ml. (N) sodium hydroxide and 25 ml. of 0.1 (N) potassium iodate. After standing for 3.5 minutes, the potassium iodide (2 gm.) was added, followed by 2.5 (N) sulphuric acid immediately and water (200 ml.). The excess iodate was then titrated with standard sodium thiosulphate using starch as indicator.

Under these conditions of excess of borohydride, the reaction was first order in ketone alone. The first order rate coefficients were determined by the expression

$$\left[ k_1 = \frac{1}{t} \ln \frac{a}{a-x} \right]$$

where 'a' is the initial ketone concentration and  $(a-x)$  is the concentration of the ketone at time 't'. The second order rate coefficient "k" was then calculated from the known standard borohydride concentration

$$k = k_1 / 4b$$

The rate constant at 40, 45 and 50°C together with the energy of activation is given in table—I.

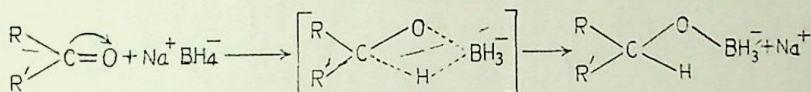
TABLE I

Temperature °C.	Concentration of chalkone.	Concentration of Sod. borohydrid e.	$k \times 10^{-2}$	E k.cal/mole.
40	0.005 (M)	0.05 (M)	4.40	
45	0.005 (M)	0.05 (M)	10.87	23.00
50	0.005 (M)	0.05 (M)	17.57	

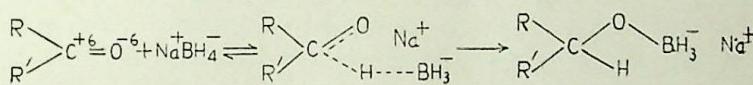
## MECHANISM OF THE REACTION

The following two mechanisms have been suggested for the reduction (K. Bowden and M. Hardy. Tetrahedron, 1966, Vol. 22, pp. 1169).

(i)



(ii)



These ion pair reactions could proceed by the direct reaction pathway (I) or by the initial formation of the complex followed by internal hydride transfer (II).

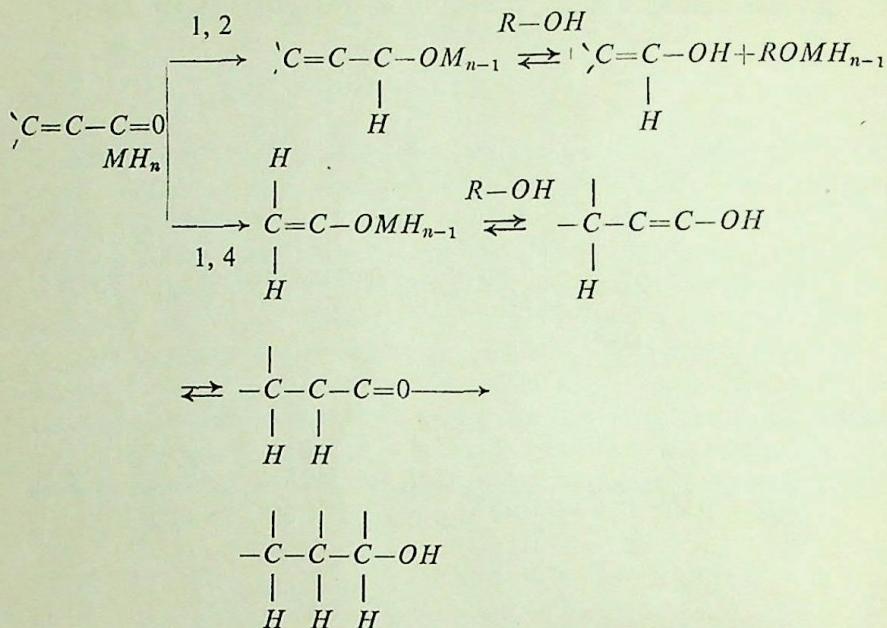
The rate of sodium borohydride reductions of acetone and acetophenone has been studied by Brown and co-workers (H. C. Brown and K. Ichikawa, J. Amer. Chem. Soc., 1962, 353). Acetophenone reacts at a slower rate ( $k=0.136 \times 10^{-4}$  litre mole $^{-1}$  Sec. $^{-1}$  at 25°C) than acetone ( $k=63 \times 10^{-4}$  litre mole $^{-1}$  sec. $^{-1}$  at 25°C). This result supports the above mechanism.

The resonance interaction of the phenyl group with the carbonyl group increases the electron density on the carbonyl group and diminishing its reactivity towards borohydride.

In case of chalkone ( $C_6H_5-CO-CH=CH-C_6H_5$ ) there is one double bond between the  $>\text{C}=0$  group and the phenyl group, which should further increase the electron density at the carbonyl group. So the rate of the reduction of the compound should be considerably slower than acetophenone. But the result is surprising, chalkone reacts faster than the acetone. This fact suggests that the above mechanism probably does not hold good in case of  $\alpha, \beta$ -unsaturated ketones.

Jackson (W. R. Jackson and A. Zurgiyah, J. Amer. Chem. Soc., 1965, 5280 ; W. R. Jackson and K. Iqbal., J. Chem. Soc. 616) have quantitatively

studied the borohydride reduction of  $\alpha, \beta$ -unsaturated ketone. They have suggested the following mechanism for the reduction.



They have attributed the fact that reduction of chalkone in isopropanol gave large amount of 1, 4-addition product with small amount of 1, 2-addition product. They have further separated the reduction product i. e., dihydrochalcone and chalcone by chromatography. The percentage of 1, 2-addition product is very low. The formation of 1, 4 addition product clearly explains the reactivity of  $\alpha, \beta$ -unsaturated ketone than acetone and acetophenone.

QUANTUM ORGANIC CHEMISTRY : PART I  
QUANTITATIVE CALCULATION OF ABSORPTION  
FREQUENCY

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Free electron gas model and molecular orbital treatment have been applied to quantitatively predict the absorption maxima, effect of replacement of  $-\text{CH}=\text{CH}-$  by  $-\text{CH}=\text{N}-$  and by  $-\text{N}=\text{N}$  of the dyes prepared from 4 : 5 diphenyl thiazole and 4-phenyl thaizole.

THE problem of setting up a quantitative theory for the light absorption of organic molecules was first attempted by Sklar<sup>1</sup> and Forster<sup>2</sup>. Herzfeld<sup>3</sup> and Sklar<sup>4,5</sup> applied these methods to polymethin dyes. Kuhn applied the concept of free electron gas, which was used by Sommerfeld for metals. Kuhn<sup>6</sup> showed that application of free electron gas model led to satisfactory interpretation of the colour of the symmetrical polymethin dyes. This method was further refined by Kuhn<sup>7</sup>. The method developed by Kuhn has been applied to quantitatively predict the absorption maxima of the dyes. The theoretical and experimental results agreed better only when 'S' atom was considered as a resonance transmitter and thus was equivalent to a vinylene analogue.

Considering the *pi* electrons of the polymethin chain to be moving in an one-dimensional box of length '*L*', where *L* is the length of the polymethin zig zag chain, the wave equation for an electron moving freely in such a potential box is given by

$$\frac{d^2\Psi}{ds^2} + \frac{8\pi^2m}{h^2} (E - Vs) \Psi = 0 \quad \dots \quad (1)$$

The limiting condition for the potential energy is,

$$V_s = 0 \text{ for } 0 < s < L$$

$$V_s = \infty \text{ for } s \geq L \text{ and } s \leq 0.$$

These limiting conditions practically confine the electron to the box.

Solving this equation, the expression for absorption maxima of symmetrical cyanine, is,

$$\lambda_{\max} = \frac{8 m c N^2 1^2}{h(N+1)} \quad \dots \quad (2)$$

Where  $m$ =mass of the electron.

$C$ =velocity of light.

$N$ =No. of  $p_i$  electrons.

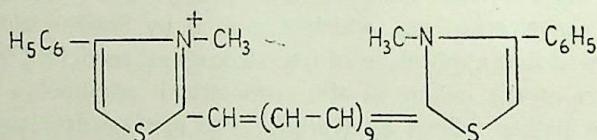
$l$ =Carbon-carbon bond distance.

$h$ =planck's constant.

In case of symmetrical cyanines derived from 4 : 5 diaryl thiiazoles, the sulphur atom can be considered equivalent to a vinylene group and thus,  $L=Nl=(2J+6) l$  where  $J$ =No. of methylene group. Kuhn<sup>8</sup> has suggested that since the  $p_i$ -electrons will go a short distance beyond the terminal atom, the value of  $L$  will be increased and by following the procedure adopted by Kuhn<sup>8</sup>, for lepidine the total length of the conjugated chain ' $L$ ' may be assigned the value of  $(2J+8) l$ . So putting  $N=2J+8$ , the  $\lambda_{\text{max}}$  value of different symmetrical cyanines have been calculated and compared with observed value. The values are given in table-1. It is observed that as the value of ' $J$ ' increases, the deviation becomes more. So further refinement is necessary.

TABLE I

$\lambda_{\text{max}}$  (Calculated and observed) values of symmetrical cyanines dirived from 4-phenyl thiazole.



Value of $j$	$\lambda_{\text{max}}$ in $\mu$	
	Theoretical ( $l=1.38 \text{ } N$ )	Experimental
1.	571.1	565.0
2.	696.0	660.0
3.	820.8	760.0

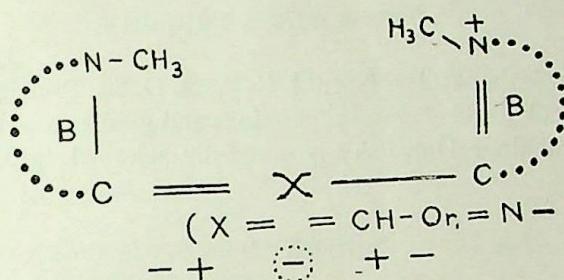
*Effect of replacement:* Kuhn<sup>9</sup> has made some generalisations on effects of hetero substitution in the polymethen chain on the spectrum. These generalisations are identical to those derived by Dewar<sup>10</sup>. These generalisations can be summarised as follows :

1. Hetero substitution raises the absorption frequency if the effected carbon atom ( $a$ ) is at position of maximum charge density in the ground state ; ( $b$ ) is at the antinode of the highest occupied orbital of the ground state.

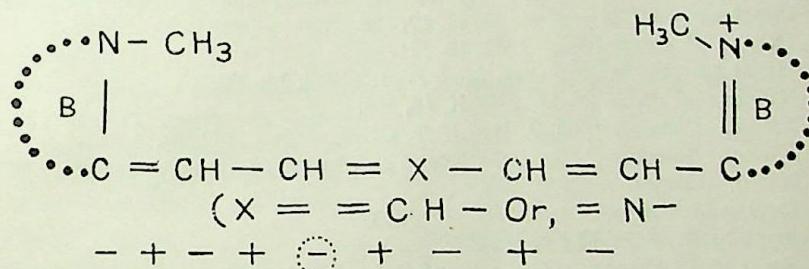
2. In the reverse case hetero substitution lowers the absorption frequency.

The structure and the sequence of the alternating charge densities in mono and penta-methin cyanines (structures I & II) are represented below :

I.



II.



The central carbon atom is relatively the seat of maximum charge density. When a nitrogen atom is substituted for the central carbon atom in the above cases, the greater positive nuclear charge caused the energy of the ground state to be lowered more than that of the excited state owing to the greater electron density at that point in the ground state. Substitution of the central carbon atom by nitrogen will, therefore, raise the absorption frequency leading to hypsochromic shift. This has been found to be so.<sup>11</sup>

This has also been satisfactorily applied to the dimethyl amino styryl dyes, their aza and diaza analogues prepared from 4 : 5 dianyl thiazoles.<sup>12</sup>

The same conclusions are also obtained by the application of M. O. theory as devised by Dewar.<sup>10</sup> The introduction of the nitrogen atom actually corresponds to replacement of an unstarred carbon atom in the carbon-ion  $R^-$  by hetero atom. Suppose the  $J$ th carbon atom in  $R^-$  is replaced to give  $R_H^-$  and the coulomb term of the hetero atom is  $q$ , relative to carbon, then to a first approximation, the change  $\delta E_r$  in the energy level [ $E_r$  will be given by the equation (3)].<sup>12</sup>

$$\delta E_r \approx -q \frac{\delta E_r}{\delta q_r} = -q a^2 r_r \quad \dots \quad (3)$$

For the highest occupied orbital in  $R^-$ ,  $a_{r_j}=0^{13}$ . This orbital remains unchanged in  $R_H^-$  to a first approximation. The energy of the first excited level in  $R_H^-$  will, from the above equation, be less than that in  $R^-$  since  $Q<0$ . Therefore, the frequency of the first absorption band (FFAB) of  $R_H^-$  is less than that of  $R^-$ . Thus bathochromic shift is caused.

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